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FINAL REPORT

FLAME RESISTANT NONTOXIC POLYMER

DEVELOPMENT

Contract No. NAS9-13802

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Prepared for

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Prepared by

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FOREWORD

This Final Report describes the work performed by Ultrasystems, Incorporated, during the period 7 January 1974 to 7 May 1975 under Contract No. NAS9-13802. The investigations were performed by K. L. Paciorek, program manager, D. W. Karle, and R. H. Kratzer. The work was administered by the NASA Lyndon B. Johnson Space Center; the technical monitor was Dr. F. S. Dawn.

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1. ABSTRACT

A number of homopolymers, copolymers, and terpolymers were synthesized employing styrene and four derivatives of diphenyl-p-styrylphosphine. Three of the basic monomers were initially developed under a previous contract; the fourth compound, derived from a commercially available intermediate, was synthesized for the first time under the current program. The various polymeric compositions were prepared by two processes, monomer bulk polymerizations and substitution of preformed polydiphenyl-p-styrylphosphine. The majority of the compositions thus produced exhibited superior melting and flame retardant characteristics as compared to polystyrene itself, but were inferior in molding and film forming capability. Terpolymerization appeared to result in the materials with the best overall combination of properties. Toxicological evaluation by NASA L. B. Johnson Space Center of three representative basic compositions in the form of molded washers showed that no mortalities occurred among the test animals exposed to the products of the oxidative thermal decomposition of the three materials. Maximum sample sizes permitted by the test equipment were used. These data confirm the results of the chemical analyses and prove the validity of developing flame resistant nontoxic polymers based on diphenyl-p-styrylphosphine compositions.

2. INTRODUCTION

Under the preceding program (1) it was established that substituted diphenyl-p-styrylphosphine derived polymers and co-polymers are promising flame retardant compositions which do not produce toxic products on thermal oxidative degradation based on quantitative analysis of the volatiles formed. Furthermore, it was shown that the variously substituted diphenyl-p-styryl-phosphines can be copolymerized with commercially used monomers as exemplified by styrene. The materials thus obtained exhibited, in addition to improved flame resistance, increased char yields and higher melting and softening characteristics making these modified polystyrenes in many of their properties superior to conventional styrene based polymers. The main drawback of all the newly developed compositions was their brittleness due to the prevalent low molecular weights.

The current program was undertaken to optimize the polymerization techniques in order to obtain high molecular weight materials amenable to conventional fabrication methods and film forming operations. The low toxicity of the thermal oxidative degradation products of diphenyl-p-styrylphosphine derived systems was determined in the past by chemical analytical means, extension of these studies to actual animal testing was necessary to supplement and confirm the analytical findings.

3. RESULTS AND DISCUSSION

The main goal of this program was to optimize the techniques previously (1) employed for the polymerization of diphenyl-p-styrylphosphine and its derivatives. In the past mainly free radical initiators were employed and the vast majority of the polymerizations was carried out in solution. Derivatives of polydiphenyl-p-styrylphosphine were obtained by substitution, e.g., oxidation, of preformed diphenyl-p-styrylphosphine polymer. The polymerization of styrylphosphine under these conditions yielded soluble, low molecular weight products in addition to varying amounts of insoluble, crosslinked materials which could not be used to prepare the desired styrylphosphine derivatives. The mechanical properties and the film forming characteristics of all products were rather poor.

During the present program the thermal bulk polymerization of diphenyl-p-styrylphosphine, its derivatives, and styrene itself, as well as bulk copolymerizations were investigated. Furthermore, a novel styrylphosphine derivative was synthesized and subjected to homo- and several copolymerizations in order to obtain end products with improved mechanical and processing characterics.

The overall program as performed embodied: (a) synthesis of candidate monomers and other intermediates; (b) polymerization and copolymerization studies, as well as characterization of the materials thus produced; (c) fabrication or molding operations, and (d) toxicological testing.

For clarity of presentation the Technical Discussion was broken into subsections as delineated above. The experimental details were omitted here since these are discussed fully in Section 4. On the other hand, chemical formulae and equations have been used

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extensively to present adequately the concepts and processes studied.
To facilitate the use of all tables and figures referred to throughout
the Technical Discussion, these have been grouped together in
consecutive order at the end of this report.

3.1   MONOMER AND INTERMEDIATE SYNTHESIS

The syntheses of the majority of the intermediates and
monomers were developed under the previous program (1), thus there
is no need to describe these here. The three main monomers were
diphenyl-p-styrylphosphine $(C_6H_5)_2PC_6H_4CH=CH_2$ and its two
pentavalent phosphorus derivatives, $(C_6H_5)_2C_3N_3-N=P(C_6H_5)_2C_6H_4CH=CH_2$
and $C_6H_5C_3N_3[N=P(C_6H_5)_2C_6H_4CH=CH_2]_2$. Although polymers
based on $(C_6H_5)_2P(O)-N=P(C_6H_5)_2C_6H_4CH=CH_2$ were described pre-
viously (1) the monomer itself could not be isolated. Additional
attempts conducted during the program failed in the preparation of the
desired product. All the reaction modes utilizing the oxidation of
diphenyl-p-styrylphosphine by diphenylphosphinyl azide gave only
the polymer, i.e.:

$$x(C_6H_5)_2P(O)N_3 + x(C_6H_5)_2PC_6H_4CH=CH_2$$

$$\downarrow$$

$$\left[(C_6H_5)_2P(O)N=P(C_6H_5)_2C_6H_4CH-CH_2\right]_x + xN_2$$
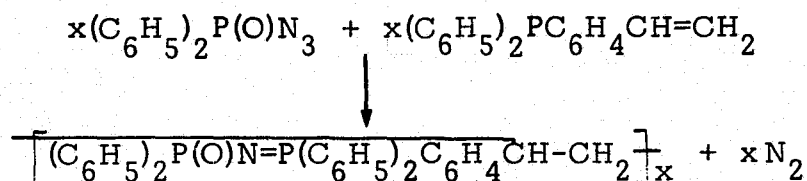
It would thus appear that during the actual oxidation a transition state
exists which activates the double bond so that it undergoes polymeri-
zation. There seems to be a relationship between the ease or rate of
oxidation of a given azide and its ability to act as a polymerization
catalyst. The triazine azides, which are very fast and effective
reactants toward trivalent phosphorus species, do not appear to
promote polymerization. Diphenylphosphoryl azide, $(C_6H_5O)_2P(O)N_3$,

whose oxidizing activity lies between that of the above phosphinyl and the triazine azides promotes polymerization, however to a much lesser degree than the phosphinyl azide. Thus the reaction of phosphoryl azide (a commercially available intermediate) and diphenyl-p-styrylphosphine did afford the novel monomer, $(C_6H_5O)_2P(O)N=P(C_6H_5)_2C_6H_4CH=CH_2$ in good yield:

$$(C_6H_5O)_2P(O)N_3 + (C_6H_5)_2PC_6H_4CH=CH_2$$

$$\downarrow$$

$$(C_6H_5O)_2P(O)N=P(C_6H_5)_2C_6H_4CH=CH_2 + N_2$$
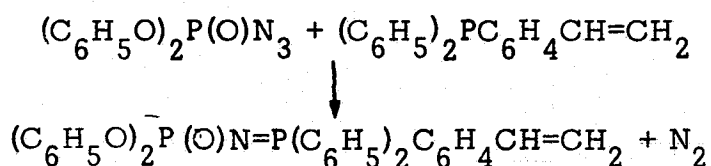
This novel monomer exhibited several desirable properties. It polymerized readily under the conditions employed and promoted the formation of relatively high molecular weight products in both homo- and copolymerizations. In addition, all polymers containing this moiety had greatly improved processing characteristics.

3.2 POLYMER FORMING REACTIONS AND POLYMER CHARACTERIZATIONS

3.2.1 Ionic Polymerizations. Ionic polymerizations were investigated as one of the potential approaches to high molecular weight materials. These were conducted on styrene to determine whether this type of process might be applicable to diphenyl-p-styrylphosphine and other monomers derived from it. The results of these studies are summarized in Table I. The procedures utilizing the $TiCl_4/(C_2H_5)_3Al$ and $TiCl_4/C_4H_9Li$ catalyst systems were partially based on disclosures by Natta (2) and Tsou (3). As it is apparent from the data listed in Table I low yields (5-22%) and low molecular weights, ($\sim$ 7000), were attained. Furthermore, this route could not be applied to diphenyl-p-styrylphosphine itself inasmuch as the workup would transform the

trivalent phosphorus into a phosphorus oxide derivative. In view of the above considerations it was decided to abandon this polymerization method.

3.2.2 <u>Bulk Polymerization</u>. The thermal polymerization of styrene in the absence of catalysts and solvents is a process widely employed in the commercial production of polystyrene. Since the catalyzed solution polymerization of diphenyl-p-styrylphosphine, which was studied during the past program (1), did not yield high molecular weight products, the bulk polymerization of diphenyl-p-styrylphosphine and its derivatives was chosen during the present study to produce flame resistant modified polystyrenes.

Kuhn (4) utilized the bulk process at relatively high temperatures and low residence times to polymerize styrene. To determine the re-producibility of his data very limited investigations were conducted on styrene itself and these are summarized in Table II. The optimum residence time, at least at 230°C, seems to be 0.75 hr. Subsequently these investigations were extended to diphenyl-p-styrylphosphine. The experiments carried out in this series are compiled in Table III. It has been found in these polymerizations that the molecular weight of the polymer did depend to a large degree on the batch of monomer used, accordingly the individual batches, from which a particular polymer was prepared, are clearly identified in Table III. The variations in product molecular weights obtained under identical con-ditions using different batches of monomer are most likely due to the presence of trace amounts of impurities, which may include unreacted starting materials used in the synthesis of diphenyl-p-styrylphosphine, solvents, and/or a polymerization inhibitor which in several instances was added to the reaction mixture during workup.

To gain a more detailed insight into the polymerization behavior of diphenyl-p-styrylphosphine differential scanning calorimetry (DSC) was employed. As can be seen in Fig. 1 the DSC scan of the monomer shows a sharp endotherm at $77^{\circ}C$, its melting point, and a very broad exotherm, which starts at $\sim 110^{\circ}C$ and extends to $230-250^{\circ}C$. This exotherm must be attributed to polymerization. The correctness of this assumption was shown by heating a sample of diphenyl-p-styrylphosphine monomer in the DSC cell to $200^{\circ}C$ (see Fig. 2) and rerunning the same sample again after cooling to room temperature (see Fig. 3). The absence in Fig. 3 of the melting endotherm at $77^{\circ}C$ and the exotherm centered at $175^{\circ}C$, which are present in Fig. 2, clearly indicate that during heating to $200^{\circ}C$ practically all monomer had been consumed.

Initially the polymerizations of diphenyl-p-styrylphosphine were conducted at $230^{\circ}C$ since at this temperature, based on DSC (see Figs. 1-3), the process appeared to be essentially complete. Comparing Runs 8, 10, and 13 (see Table III), which were performed with one batch of monomer at one temperature for different lengths of time, a 0.75 hr residence time would seem to yield the best product insofar as the molecular weight is concerned. This is in good agreement with the styrene findings (see Table II). The low molecular weight exhibited by the material obtained in Test No. 13 is probably due to the polymer workup since here a relatively large sample was precipitated into a comparatively small volume of heptane which allowed entrapment of low molecular weight components.

Tests 18, 20, and 19 (Table III) were performed at different temperatures for the same period of time; under these conditions the lowest temperature, $180^{\circ}C$, afforded the highest molecular weight product. It has to be noted that this particular series of experiments

was performed again with only one batch of monomer, a different batch than that used in Runs 8, 10, and 13 described above. None of the polymers exhibited molecular weights of the magnitude required for film fabrication.

Consultation with experts in commercial polystyrene manufacturing (5) revealed that high molecular weight material is obtained by a bulk process utilizing relatively low temperatures for extended periods of time. It is apparent from Run Nos. 24, 26, and 27, conducted at 100°C for 24, 8, and 1 hr, respectively, that this method unfortunately cannot be applied to the polymerization of diphenyl-p-styrylphosphine. Long reaction times (Run Nos. 24 and 26) gave mainly gelled (crosslinked) material, whereas short reaction times resulted in low conversions and low molecular weight products. The reason for the predominant formation of highly crosslinked polymers using prolonged reaction times is attributed to chain transfer reactions initiated by the trivalent phosphorus atom present in diphenyl-p-styrylphosphine.

As noted in Section 4, diphenyl-p-styrylphosphine was initially prepared in the presence of an inhibitor to avoid premature polymerization. During the current program the synthesis was modified and good yields of the product were realized without using such an additive. Apparently when an inhibitor was employed, even after several crystallizations, traces remained in the purified monomer which impaired the polymerization process (compare Run 28 with Runs 18 or 29).

Based on the results obtained to date the optimum polymerization conditions for producing high molecular weight diphenyl-p-styrylphosphine have not been definitely established. Yet, it is tempting to speculate that conducting the reaction in the vicinity of

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180°C for longer periods of time than investigated under the current program and using diphenyl-p-styrylphosphine prepared without the use of an inhibitor would give a polymer exhibiting the required characteristics.

In addition to the just described study of the bulk polymerization of diphenyl-p-styrylphosphine it was an objective of this program to prepare polymers and copolymers using pre-oxidized derivatives of monomeric diphenyl-p-styrylphosphine. The three candidate monomers for these investigations were:

$$(C_6H_5O)_2P(O)N=P(C_6H_5)_2C_6H_4CH=CH_2 \; ,$$

$$(C_6H_5)_2C_3N_3N=P(C_6H_5)_2C_6H_4CH=CH_2 \; , \; \text{and}$$

$$(C_6H_5)C_3N_3[N=P(C_6H_5)_2C_6H_4CH=CH_2]_2 .$$
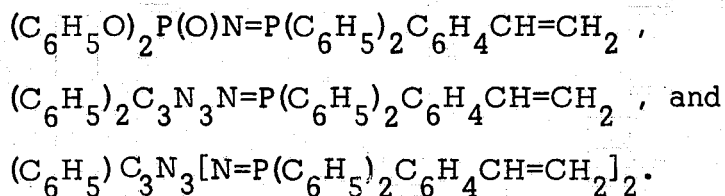
In view of the different substituents present it was to be expected that the optimum polymerization parameters will be different for each of these compounds. To determine the temperature to be employed in the bulk polymerizations differential scanning calorimetry (DSC) was utilized to a great extent in a manner parallel to that discussed above for diphenyl-p-styrylphosphine itself. The bulk homopolymerizations performed are listed in Table IV, whereas the copolymerizations are presented in Table V.

The monomer derived from the oxidation of diphenyl-p-styrylphosphine with diphenylphosphoryl azide (see Section 3.1), $(C_6H_5O)_2P(O)N=P(C_6H_5)_2C_6H_4CH=CH_2$, appeared to undergo polymerization in the vicinity of its melting point, $\sim 150^{\circ}$C, as can be seen from Fig. 4. Heating a given monomer sample up to 200°C in the DSC cell followed (after cooling) by a repeat scan gave a trace essentially identical with that shown in Fig. 3. The absence of any exotherms and endotherms in the 25-250°C range

would indicate the absence of melting which is not surprising

since all monomer has been consumed and the melting ranges

reported for the polymeric compositions (Run Nos. 11, 25, 30,

31, and 35; Table IV) are very wide and are not crystalline melt-

ing points. The molecular weights attained under the different

conditions employed varied from ca 50,000 to > 100,000. In

the main temperature range investigated for polymerization,

150-165°C, no evident trends were detected insofar as the

process duration is concerned. On the other hand it is clear that

at temperatures as high as 230°C (Run No. 11, Table IV) cross-

linking does occur. From the DSC scan, (see Fig. 4), it can be

deduced that the polymerization process peaks at 165°C thus the

use of higher temperatures might very well result in the occurrence

of side reactions.

Out of all the polymers studied under this program

$\overline{[(C_6H_5O)_2P(O)(C_6H_5)_2C_6H_4}CH-CH_2]_x$ afforded the materials

most readily processible into moldings and films. However, its

melting or softening range was too low for the program require-

ments. The copolymerization with other monomers was visualized

as the best route to improve these properties; these investigations

will be described later in this section.

Thermogravimetric analysis (TGA) reveals that this type

of polymers do not lose weight and are oxidatively stable

to ~ 275°C. Comparing Figs. 5 and 6 it can be seen, however,

that minor differences in regard to oxidative thermal stability

between samples do exist. These two materials are of identical

elemental composition (see Run No. 30, Table VI, and Run No. 35,

Table VII), although the product from Run 30 has roughly twice

the molecular weight than the material formed in Run 35 (see

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Table IV). On this basis one would expect the material from Run 30 (Fig. 5) to be thermally more stable than that from Run 35 (Fig. 6). Yet, comparing Figs. 5 and 6 it is evident that the degrees in stability are opposite to those expected. This discrepancy cannot be explained at present.

Only a very limited number of experiments was performed on the bulk homopolymerization of the $(C_6H_5)C_3N_3[N=P(C_6H_5)_2C_6H_4CH=CH_2]_2$ monomer inasmuch as this material in view of its difunctionality has to form highly crosslinked polymers. Although the monomer does show on visual observation a melting point at $122°C$, accompanied by polymerization, in the DSC scan the melting endotherm is absent (see Fig. 7). What appears to be a polymerizarion exotherm starts at $\sim 115°C$ and peaks at $190°C$. Heating of the monomer at $130°C$ for 5 hr afforded a trace of gel, the bulk of the sample was composed essentially of the starting material (see Run 32, Table IV). Conducting the process at $160°C$ (see Run 33, Table IV) afforded mainly a chloroform insoluble highly crosslinked polymer. The TGA curve, given in Fig. 8, shows this polymer to undergo initial slight weight loss around $50°C$, which is most likely due to entrapped solvent. The actual decomposition appears to start at ca $300°C$; it is noteworthy, however, that the char yield stabilizes at 41% at $\sim 550°C$ and does not seem to decrease further up to $610°C$.

The monomer $(C_6H_5)_2C_3N_3N=P(C_6H_5)_2C_6H_4CH=CH_2$ exhibits clearly in its DSC scan a melting endotherm at $175°C$ (see Fig. 9) which is followed by an exotherm with a maximum at $\sim 220°C$. Based on the above the polymerization should be completed only at ~ 225-$250°C$. Yet, it is revealing that

polymerization must occur to a sufficient degree below 200°C to consume most of the originally present monomer. This becomes evident from comparing Figs. 10 and 11. The DSC scan shown in Fig. 10 is that of $(C_6H_5)_2C_3N_3$-N=$P(C_6H_5)_2C_6H_4CH$=CH_2 monomer and exhibits a sharp melting endotherm at 171°C. When the same sample was rerun after first heating to 200°C and then cooling to room temperature, no melting endotherm could be observed (see Fig. 11). This indicates that practically all monomer had been consumed probably via forming low molecular weight oligomers, whereas the information from the DSC scan shown in Fig. 9 indicates that exothermic polymerization reaches its highest rate only at $\sim 220^{\circ}$C.

Subjecting the monomer to thermal polymerization at 190° and 230°C for varying periods of time (Run Nos. 36, 37, 38, and 41, Table IV) failed to give high or even moderate molecular weight materials. The elemental analysis of a representative polymer sample (see Run No. 38, Table VI) shows that no decomposition or side reaction took place on polymerization. It could very well be that the relatively high melting characteristics of the resultant polymer prevent the formation of higher molecular weight materials under these conditions.

The thermal gravimetric behavior of the bulk prepared polymer $\left[(C_6H_5)_2C_3N_3N=P(C_6H_5)_2C_6H_4CH-CH_2\right]_x$ (see Fig. 12) corresponded closely to that of the material obtained by substitution of preformed polymer reported previously (Fig. 24 in reference 1); however, the material obtained from polymerization of substituted monomer exhibited a somewhat higher decomposition onset and char yield. Attempts to fabricate or mold the homopolymer all ended in failure which is not surprising in view of the unacceptably low molecular weights which were invariably attained.

Copolymerization allows some tailoring of the final product properties by selection of specific monomers and their relative ratios. The main difficulty in this type of a process is the ease of copolymerization as compared to homopolymerization and the formation of true random copolymers and not block copolymers. On the other hand in certain instances, copolymers can be obtained from monomers which by themselves do not polymerize under the same conditions.

From the homopolymerization studies described above it became apparent that copolymerization was one of the possible avenues to make the candidate polymers more amenable to fabrication and also to improve their melting characteristics. In Table V are listed the bulk copolymerizations performed during the current program. The Tests 9 and 16 were conducted employing styrene itself as one of the copolymers to test the feasibility of preparing materials using commercial monomers. The elemental analysis of the resultant polymer (see Run 9, Table VI) proves the validity of this process. It was speculated that copolymerization of $(C_6H_5O)_2P(O)N=P(C_6H_5)_2C_6H_4CH=CH_2$ with the difunctional monomer $(C_6H_5)C_3N_3[N=P(C_6H_5)_2C_6H_4CH=CH_2]_2$ would yield a facile to fabricate material exhibiting acceptable melting characteristics. The latter aim was fulfilled; unfortunately the major product afforded in 82% yield (see Run 34, Table V) proved to be highly crosslinked thus insoluble in common organic solvents and not amenable to film casting. It is noteworthy that its TGA curve (Fig. 13) is closely reminiscent of that of the homopolymer (see Fig. 6). A small quantity (4% yield) of chloroform soluble material which was isolated appeared to consist essentially of

$$\left[(C_6H_5O)_2P(O)N=P(C_6H_5)_2C_6H_4CH-CH_2 \right]_x.$$
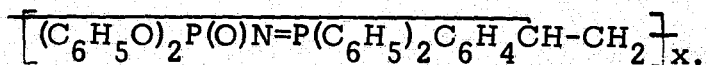
The copolymerization of diphenyl-p-styrylphosphine and $(C_6H_5)_2C_3N_3N=P(C_6H_5)_2C_6H_4CH=CH_2$ (Run No. 39, Table V) gave a higher molecular weight material than that obtained by homopolymerization of the triazine substituted monomer; consequently it would seem that this particular process can be optimized to give a practical system. The thermal stability of this copolymer is comparable to that of the triazine containing homopolymer (compare Fig. Nos. 14 and 12).

In the copolymerization of

$(C_6H_5)C_3N_3\left[N=P(C_6H_5)_2C_6H_4CH=CH_2\right]_2$ and
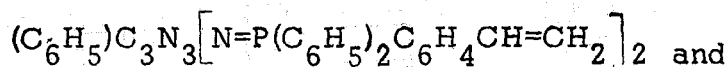
$(C_6H_5)_2C_3N_3N=P(C_6H_5)C_6H_4CH=CH_2$ soluble and insoluble polymers were obtained (see Runs 40 and 44, Table V). The soluble portions appeared to consist of the homopolymer

$$\left[(C_6H_5)_2C_3N_3N=P(C_6H_5)_2\ C_6H_4CH-CH_2\right]_x$$
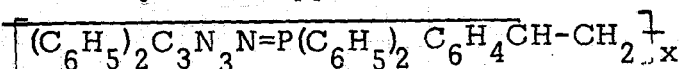
as shown by the melting characteristics, infrared spectra, and TGA curves (compare Figs. 15 and 12). The insoluble fractions exhibited definitely higher melting characteristics, yet the TGA curves (see Figs. 16 and 17) were virtually identical with those of the homopolymers $\left[(C_6H_5)_2C_3N_3N=P(C_6H_5)_2C_6H_4CH-CH_2\right]_x$. In both of the curves (Figs. 16 and 17) a weight loss is evident $\sim 200^{\circ}C$. This is believed to be due to the liberation of the solvent entrapped in the gelled polymer; the elemental analysis (see Table VII, Run 44) supports this postulation. These polymers in contrast to the homopolymers $\left[(C_6H_5)_2C_3N_3N=P(C_6H_5)_2C_6H_4CH-CH_2\right]_x$ could be molded.

The last two copolymerizations listed in Table V were performed to compare the characteristics of bulk produced terpolymers with those obtained by "oxidation" (substitution) of preformed polydiphenyl-p-styrylphosphine. For ease of comparison of the
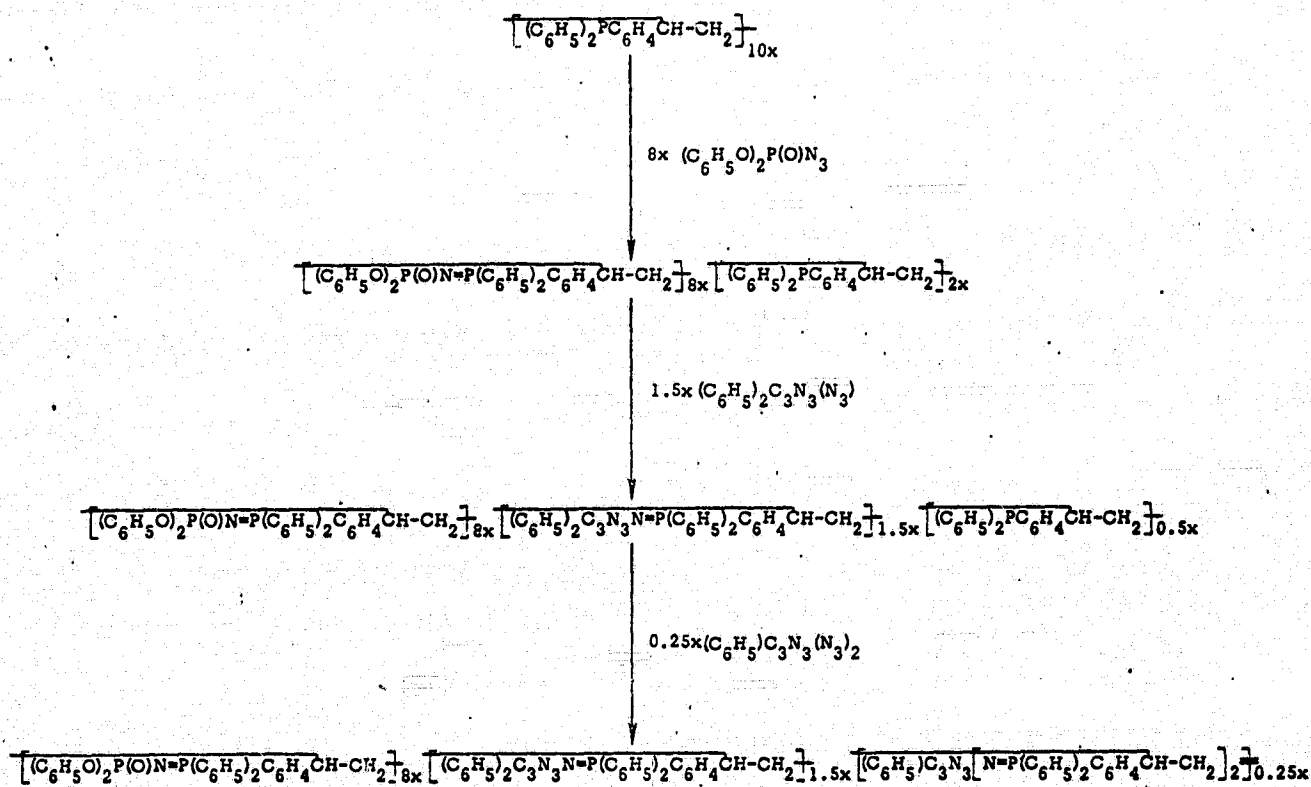
data it seemed best to discuss these systems together in the subsection 3.2.3.

3.2.3   Substitution of preformed polydiphenyl-p-styrylphosphine.

As was delineated previously, the two methods employed under the current program to prepare homo-, co-, and terpolymers were: a) bulk polymerization of monomers, and b) substitution ("oxidation") of preformed diphenyl-p-styrylphosphine polymer. The latter procedure had been utilized to a limited extent in the past (1), mainly in the synthesis of homopolymers with some efforts being directed at chain extension reactions. Under the current program a number of copolymers and terpolymers were synthesized and these are presented in Table VIII. The only homopolymer described is the one derived from the oxidation of diphenyl-p-styrylphosphine with diphenylphosphoryl azide. This particular polymer system was not prepared previously thus it was of interest to compare the properties of the material obtained by polymerization of the monomer with those of the material produced by substitution of the preformed polymer. Based on the melting characteristics and TGA data (see Run Nos. 25, 30, and 35, Table IV, and Run A, Table VIII, also compare Figs. 6 and 21) the materials are closely comparable. Apparently, the substitution process is accompanied by further polymerization of polydiphenyl-p-styrylphosphine, inasmuch as the final polymer contained 93 repeating units whereas in the starting material this number was 39. This finding is actually not surprising since, as described in Section 3.1, the substitution of diphenyl-p-styrylphosphine monomer itself is accompanied by some polymerization. Diphenylphosphinyl azide exhibits similar behavior except to a larger degree than diphenylphosphoryl azide, which prevented the isolation of the $(C_6H_5)_2P(O)N=P(C_6H_5)_2C_6H_4CH=CH_2$ monomer (see Section 3.1).

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The polymer described in Run B, Table VIII was prepared specifically for toxicological testing; the reason for synthesizing the copolymer was the relatively sluggish reaction of diphenyl-phosphinyl azide which tends to result in an incomplete oxidation. To avoid this the required quantity of 2,4-diphenyl-6-azido-s-triazine was added toward the end of the reaction (see the Experimental Section).

The terpolymers obtained in Runs C to I (Table VIII) were specifically prepared to determine the optimum proportion of the difunctional entity necessary to prepare high molecular weight, high melting, yet soluble compositions. The majority of the experiments (Runs E to I) were conducted using diphenylphosphoryl azide since this substituent gives materials most amenable to fabrication and film casting; in addition diphenylphosphoryl azide is commercially available. The overall process can be best represented by the sequence delineated below:

$$[(C_6H_5)_2PC_6H_4CH-CH_2]_{10x}$$

$$8x \ (C_6H_5O)_2P(O)N_3$$

$$[(C_6H_5O)_2P(O)N=P(C_6H_5)_2C_6H_4CH-CH_2]_{8x}[(C_6H_5)_2PC_6H_4CH-CH_2]_{2x}$$

$$1.5x \ (C_6H_5)_2C_3N_3(N_3)$$

$$[(C_6H_5O)_2P(O)N=P(C_6H_5)_2C_6H_4CH-CH_2]_{8x}[(C_6H_5)_2C_3N_3N=P(C_6H_5)_2C_6H_4CH-CH_2]_{1.5x}[(C_6H_5)_2PC_6H_4CH-CH_2]_{0.5x}$$

$$0.25x(C_6H_5)C_3N_3(N_3)_2$$

$$[(C_6H_5O)_2P(O)N=P(C_6H_5)_2C_6H_4CH-CH_2]_{8x}[(C_6H_5)_2C_3N_3N=P(C_6H_5)_2C_6H_4CH-CH_2]_{1.5x}[(C_6H_5)C_3N_3[N=P(C_6H_5)_2C_6H_4CH-CH_2]_2]_{0.25x}$$

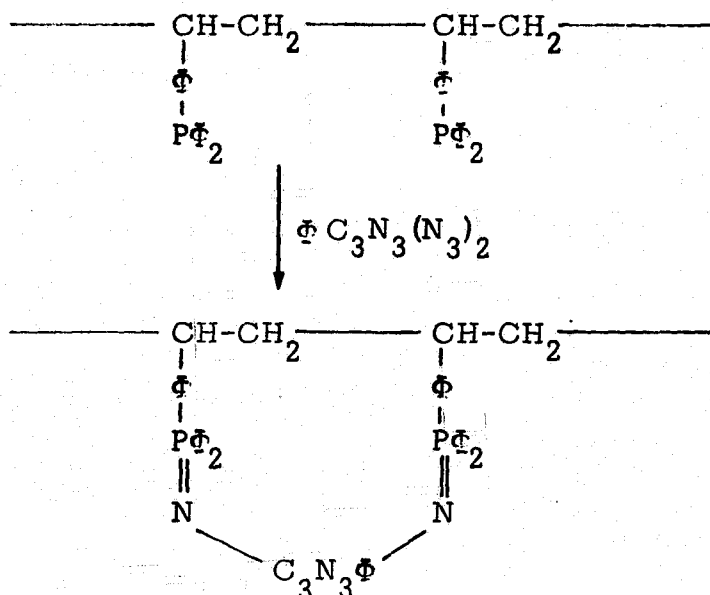It has to be understood that this sequence does not portray exactly the mode of addition, since not all of the 2-azido-4,6-diphenyl-s-triazine is added in step 2. Actually the reaction is performed in four stages and this is clearly described in the Experimental Section. The reason for this operation was to ensure that when the diazide is introduced there are still sufficient number of sites present to allow interchain linking to take place, yet not enough free sites for intramolecular reaction, i.e., it is desirable to have scheme I to operate, not scheme II. (It should also be noted that the above representation does not imply that block copolymers have been formed.)

Scheme I:

$$2 \longrightarrow \overset{\displaystyle |}{\underset{\displaystyle |}{CH}}-CH_2 \longrightarrow$$

$$\Phi$$

$$P\Phi_2$$

$$\downarrow \quad \Phi C_3N_3(N_3)_2$$

$$\longrightarrow \overset{\displaystyle |}{\underset{\displaystyle |}{CH}}-CH_2 \longrightarrow$$

$$\Phi$$

$$\overset{\parallel}{P\Phi_2}$$

$$N$$

$$C_3N_3\Phi$$

$$N$$

$$\overset{\parallel}{P\Phi_2}$$

$$\Phi$$

$$\longrightarrow CH-CH_2 \longrightarrow$$

Scheme II:

$$
\begin{array}{ccc}
\text{------CH-CH}_2\text{------} & \text{------CH-CH}_2\text{------} \\
\quad | & \quad | \\
\quad \Phi & \quad \Phi \\
\quad | & \quad | \\
\quad P\Phi_2 & \quad P\Phi_2
\end{array}
$$

$$\downarrow \; \Phi\,C_3N_3(N_3)_2$$

$$
\begin{array}{ccc}
\text{------CH-CH}_2\text{------} & \text{------CH-CH}_2\text{------} \\
\quad | & \quad | \\
\quad \Phi & \quad \Phi \\
\quad | & \quad | \\
\quad P\Phi_2 & \quad P\Phi_2 \\
\quad \| & \quad \| \\
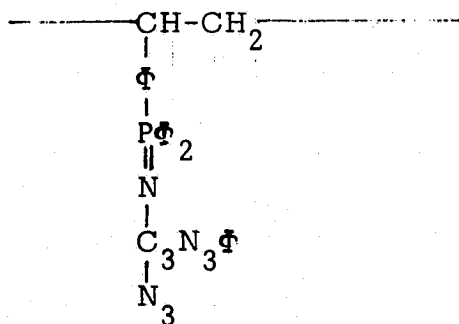\quad N & \quad N \\
\end{array}
$$
$$\diagdown\; C_3N_3\Phi\; \diagup$$
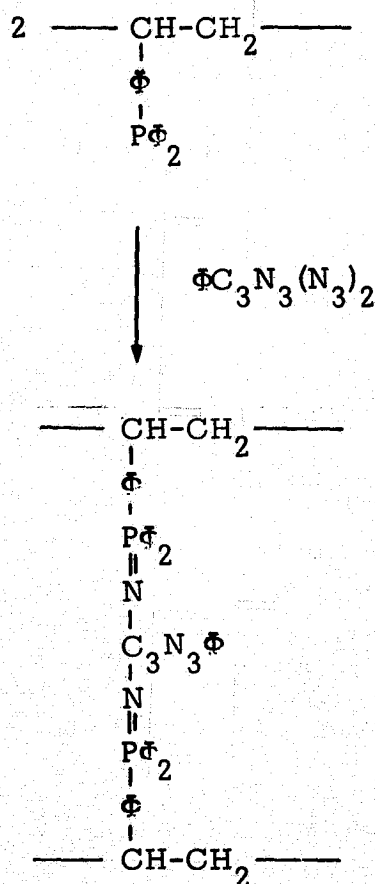
It is obvious that in tests C and E the concentration of the diazide employed was too high resulting in a densely crosslinked network and thus insoluble end product. To obtain the higher melting characteristic required in the final material the proportion of 2-azido-4,6-diphenyl-s-triazine was increased and that of the phosphorus azides was proportionately decreased. The compositions listed in Runs F to I were thus tailored with the specific objective to synthesize a soluble polymer of relatively high molecular weight and acceptable melting characteristics. To a degree, this was achieved in material I; however as can be seen the number of repeating units was not increased as compared to that of the starting material pointing to absence of chain extensions. Examining the elemental analysis data for the material produced in Run H (see Table VI) the higher than expected nitrogen value indicates the presence of structures containing unreacted azido-moieties, e.g.:

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$$-\text{---}\underset{\underset{\underset{\underset{\underset{\underset{N_3}{|}}{C_3N_3\Phi}}{|}}{N}}{\overset{\parallel}{P\Phi_2}}}{\underset{|}{\overset{|}{\Phi}}}{\overset{|}{CH}}-CH_2\text{---}$$

which supports the molecular weight data. It is believed that this can be rectified by adjusting the experimental conditions, i.e., addition mode; however, this is a trial and error type of an undertaking. On the other hand once the procedure is established it should be hopefully readily reproducible.

To evaluate possible differences in physical properties and stability characteristics between materials prepared by bulk polymerization and those obtained via "oxidation" of preformed polymer two compositions were produced using both methods. The bulk polymerized products were obtained in Runs 43 and 46, Table V, the materials of identical composition obtained by "oxidizing" preformed poly(diphenyl-p-styrylphosphine) are described in Runs E and I, Table VIII. Both of these were terpolymers and the differences between them (Run 43 and Run E versus Run 46 and Run I) were the concentrations of the difunctional moiety,
$(C_6H_5)C_3N_3[N=P(C_6H_5)_2C_6H_4CH=CH_2]_2$.
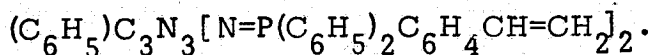
The polymers obtained in Runs 43 and E were both insoluble. Although the TGA curves (compare Figs. 19 and 25) and the infrared spectra appear to be identical the melting characteristics of the material prepared by bulk polymerization (Run 43) indicates a more highly crosslinked structure than that present in the product obtained via "oxidation" of preformed polymer (Run E). In order to obtain soluble products the concentration of the above mentioned difunctional component was therefore decreased in Runs 46 and I.

Examining Tables V (for Run 46) and VIII (for Run I) it can be seen
that the bulk polymerization process (Run 46) favors crosslinking
as evidenced by insolubility and melting characteristics, whereas
the "oxidation" of preformed polymer (Run I) produces a soluble
material of identical composition. It is noteworthy that the polymer
prepared by bulk polymerization (Run 46, Fig. 20) exhibits a
higher char yield above 450°C than the material obtained via
"oxidation" of preformed polymer (Run I, Fig. 29), which is in
agreement with the conclusion that the bulk polymerized product
is highly crosslinked and therefore insoluble. The fact, that the
product from Run I is soluble would then indicate that either the
degree of crosslinking is not sufficient to cause insolubility or
that the reaction of the difunctional crosslinking agent was in-
complete as discussed above for Run H. In the bulk terpolymerizations
(Runs 43 and 46, Table V) the insoluble material accounted for the
major portion of the product; based on the infrared spectra and melt-
ing characteristics the soluble portions consisted of the homo-
polymer $\left[(C_6H_5O)_2 P(O)N=P(C_6H_5)_2 C_6H_4 CH-CH_2 \right]_x$.

In view of the findings presented above it is tempting to
postulate that very promising polymer systems should result from a
continuation of the bulk copolymerization of selected monomers,
including a certain proportion of diphenyl-p-styrylphosphine, follow-
ed by solution crosslinking with 2,4-diazido-6-phenyl-s-triazine.
To a degree it has been established that inclusion of the difunctional
monomer $(C_6H_5)C_3N_3[N=P(C_6H_5)_2 C_6H_4 CH=CH_2]_2$ in the polymerization
mixture gives invariably insoluble products. Yet it cannot be ignored
that it might be possible to form a workable composition by using
only a very small quantity of the difunctional moiety. Unfortunately,
this does not seem to be readily accomplished. Another approach would
be to admix with a copolymer, such as the one delineated above, a

small quantity of 2,4-diazido-6-phenyl-s-triazine prior to film casting and then conduct the actual crosslinking (cure) on the film itself. It can be seen that a number of options are available and it is believed that at least some of these will result in practical polymer systems.

3.3 MOLDING AND FABRICATION STUDIES

A number of polymeric compositions prepared under this contract were subjected to molding operations using a mold, presented in Fig. 30, in conjunction with a Carver Laboratory
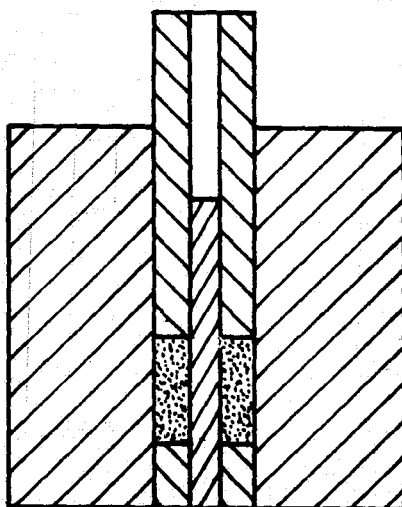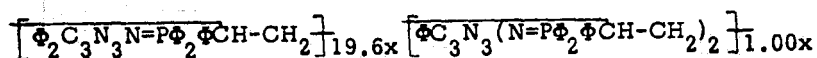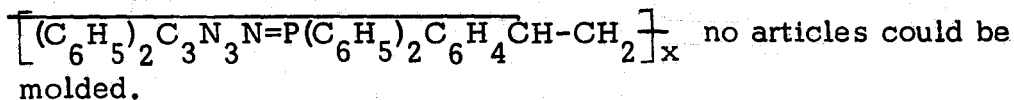
Figure 30:

Mold for compressions sintering. Dimensions of washers produced are 17 mm O.D., 5 mm I.D., various heights.

Press Model C. The representative molding operations are summarized in Table IX. The first three examples given pertain to the preparation of washers for toxicological testing by L. B. Johnson Space Center. The conditions delineated are those found optimum for the production of a relatively large number of uniform washers. The first two polymers afforded molded products which exhibited

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good material integrity, the copolymer

$$\left[\Phi_2 C_3 N_3 N{=}P\Phi_2 \Phi CH{-}CH_2\right]_{19.6x}\left[\Phi C_3 N_3 (N{=}P\Phi_2 \Phi CH{-}CH_2)_2\right]_{1.00x}$$

gave very brittle discs whereas from the homopolymer

$\left[(C_6H_5)_2 C_3 N_3 N{=}P(C_6H_5)_2 C_6 H_4 CH{-}CH_2\right]_x$ no articles could be molded.

The homopolymer $\left[(C_6H_5O)_2 P(O)N{=}P(C_6H_5)_2 C_6 H_4 CH{-}CH_2\right]_x$ could be readily molded into a shaped article (washer) and formed promising films both on pressing in the press and from solution on a 32 mil aluminum plate. The main drawback of these compositions were their low melting characteristics. As was discussed in sub-sections 3.2.2 and 3.2.3 a number of copolymer systems involving the monomer $(C_6H_5O)_2 P(O)N{=}P(C_6H_5)_2 C_6 H_4 CH{=}CH_2$ were investigated by selective "oxidation" of diphenyl-p-styrylphosphine-polymer (see Table VIII). This is illustrated by terpolymer E, listed as the last entry of Table IX, which formed the best washer insofar as mechanical properties are concerned.

Clear, relatively well adhering films have been cast from copolymers F, G, and I (these materials are listed in Table VIII) using 2-10% solutions in either tetrahydrofuran or chloroform. In some instances room temperature drying was followed by heat treatment or curing at 260°F. Composition F gave probably the most promising film regarding clarity, adhesion, and continuity. Additional material optimization is however necessary to improve the melting characteristics and abrasion resistance.
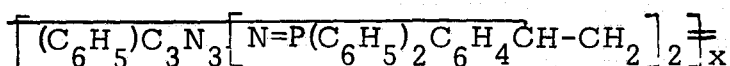
3.4   TOXICOLOGICAL TESTING
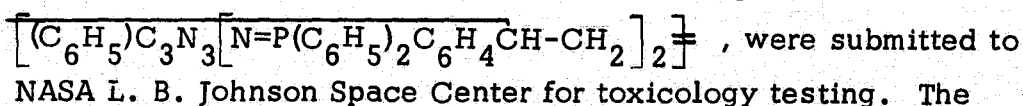
Under this program three basic polymer systems, namely:
$\left[(C_6H_5)_2 P(O)N{=}P(C_6H_5)_2 C_6 H_4 CH{-}CH_2\right]_x$,

$$\left[(C_6H_5O)_2P(O)N=P(C_6H_5)_2C_6H_4CH-CH_2\right]_x \quad \text{and}$$

$$\left[(C_6H_5)_2C_3N_3N=P(C_6H_5)_2C_6H_4CH-CH_2\right]_x$$
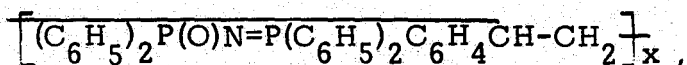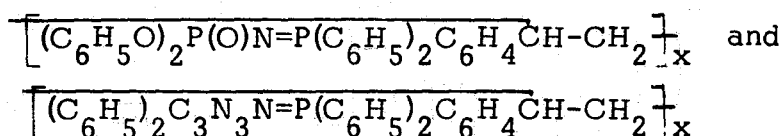
were developed. The fourth potential polymer

$$\left[(C_6H_5)C_3N_3\left[N=P(C_6H_5)_2C_6H_4CH-CH_2\right]_2\right]_x$$

does not represent a separate entity since it is of a very similar nature as the third of the above listed compositions. In addition, it is of no practical interest as a homopolymer due to the difunctional nature of the original monomer which leads to a highly crosslinked, insoluble end product. Consequently it can be utilized only as comonomer in low concentrations.

The polymer systems depicted above, with the exception of the material substituted with the diphenylphosphoryl moiety, i.e., $\left[(C_6H_5O)_2P(O)N=P(C_6H_5)_2C_6H_4CH-CH_2\right]_x$, which was only recently developed, were subjected under a previous program (1) to thermal oxidative degradation followed by analyses of the liberated room temperature volatiles. The only products detected were carbon dioxide, carbon monoxide, and benzene. Thus it could be assumed that these compositions did not present a danger insofar as the formation of toxic products upon oxidative thermal decomposition is concerned; however, this stipulation was based only on chemical analytical data. For valid conclusions animal tests performed by another laboratory were mandatory.

Accordingly three samples representing the three general polymer systems, including two polymers containing certain amounts of the difunctional crosslinking moiety $\left[(C_6H_5)C_3N_3\left[N=P(C_6H_5)_2C_6H_4CH-CH_2\right]_2\right]$, were submitted to NASA L. B. Johnson Space Center for toxicology testing. The

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elemental compositions of these test specimens are given in Table VII. Each polymer sample was composed of 20-27 washers of O.D. 0.709" with a center hole of I.D. 0.25" and 0.08" average thickness. These washers were fabricated using the apparatus and procedures described in Section 3.3. The amounts of materials submitted varied between 9.25 g and 13.10 g, which were sufficient for two tests on each of the three compositions. Copies of the original test reports, to which references to the tables of this report as well as details on compositions have been added, are given in the following three pages.

The results of these tests support the analytical findings and show clearly that the materials developed under the current program do not pose any toxic danger on thermal oxidative degradation. In view of this and the physical and flame retardant characteristics of these compositions, further efforts in optimizing these systems would seem well justified.

NORTHROP Services, Inc.

A Subsidiary of Northrop Corporation

0049-750-03.12

P.O. BOX 34416
HOUSTON, TEXAS 77034
713/488-2500

22 October 1974

TO: W. J. Rippstein, Jr.

FROM: D. A. Bafus, Ph.D.
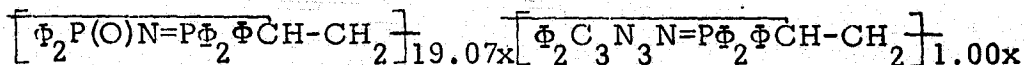
SUBJECT: Ultrasystems Polystyrene

The Toxicology Laboratory of Northrop Services, Incorporated has conducted limited studies on the pyrolysis of Polystyrene (Sample No. 1-74-56-2) prepared by Ultrasystems, Incorporated. The onset to thermal degradation in air was estimated to be $669^{\circ}K\pm5^{\circ}$ ($396^{\circ}C$) by thermal gravimetric analysis while at $729^{\circ}K\pm5^{\circ}$ ($456^{\circ}C$) the pyrolysis is about 70% completed.

Two samples of 3.0 and 6.82g were pyrolyzed in air at $823^{\circ}K$ with no mortalities recorded. An atmospheric sample of the 3.0g pyrolysis was analyzed for carbon monoxide and it was found to be 515 mg/m³ (400ppm). No CO analysis was performed on the atmosphere from the 6.82g pyrolysis because of analytical instrumentation problems.

D. A. Bafus

D. A. Bafus, Ph.D.
Toxicology Section
Space Sciences Laboratory

Composition of sample:

$$\left[\Phi_2 P(O)N=P\Phi_2\Phi CH-CH_2\right]_{19.07x}\left[\Phi_2 C_3 N_3 N=P\Phi_2\Phi CH-CH_2\right]_{1.00x}$$

For details see Tables VII & VIII

NORTHROP Services, Inc.

A Subsidiary of Northrop Corporation

12 November 1974

P.O. BOX 34416
HOUSTON, TEXAS 77034
713/488-2500

NASA/JSC OSS
NAS 9-13000
0053-750-03.12

National Aeronautics and Space Administration
Lyndon B. Johnson Space Center
Houston, Texas 77058

Attention: Mr. W. J. Rippstein, Jr./DD6

Gentlemen:

Subject: Ultrasystems Poly-p-(Diphenylphosphino) Styrene

The Toxicology Laboratory of Northrop Services, Incorporated has conducted limited studies on the pyrolysis of the polystyrene (sample no. 1-74-115-4) prepared by Ultrasystems, Incorporated. The onset to thermal degradation in air was estimated to be 664 ± 5°K (391°C) by thermal gravimetric analysis, while at 756 ± 5°K (483°C) the pyrolysis is about 76% completed.

Two samples of 3.0 and 5.34g were pyrolyzed in air at 773°K with no mortalities recorded. Atmospheric samples were analyzed for carbon monoxide and the carbon monoxide concentrations were found to be 393 mg/m^3 (305ppm) and 174 mg/m^3 (174 ppm) respectively.
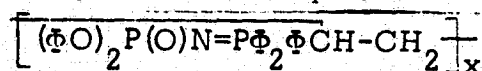
Sincerely yours,

Northrop Services, Incorporated

D. A. Bafus, Ph.D.
Toxicology Section
Space Sciences Laboratory

DAB:blm

cc: C. J. Hodapp, Ph.D.

Composition of sample:

$$\left[(\Phi O)_2 P(O)N=P\Phi_2\Phi CH-CH_2 \right]_x$$

For details see Tables IV and VII

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Attn: W.J. Rippstein

Subject: Ultrasystems 2-Azido-4,6-Diphenylphosphino Poly-P-Styrene

The Toxicology Laboratory of Northrop Services, Inc. conducted
limited pyrolysis studies on the polystyrene (sample no. 1-74-137-3)
prepared by Ultrasystems, Inc. The onset to thermal degradation in
air was estimated to be $683° \pm 5°K$ ($410°C$) by Thermal Gravimetric
Analysis. Further sharp changes in weight loss were observed at
$744° \pm 5°K$ ($471°C$, 70% completion), $919° \pm 5°K$ ($646°C$, 90% completion),
and $1215° \pm 5°K$ ($942°C$, and 100% completed).

Two samples of 3.0 and 5.27 g were pyrolyzed in air at $823° \pm 5°K$
($550°C$) with no mortalities observed from one-half hour exposure.
The carbon monoxide concentrations found in the atmospheric samples
were 348 mg/m^3 (270 ppm, 3.0 g) and 683 mg/m^3 (530 ppm, 5.27 g).

Sincerely yours,

Donald A Bafus

Composition of sample:

$$\left[\Phi_2 C_3 N_3 N=P\Phi_2 \Phi CH-CH_2 \right]_{19.6x} \left[\Phi C_3 N_3 (N=P\Phi_2 \Phi CH-CH_2)_2 \right]_{1.00x}$$
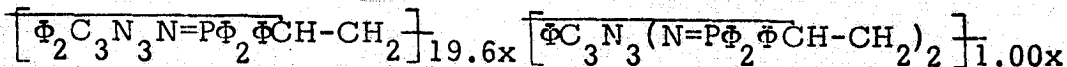
For details see Tables V and VII

4. EXPERIMENTAL

All solvents used were reagent grade and were dried and distilled prior to use. All operations involving moisture or air sensitive materials were carried out either in an inert atmosphere enclosure (Vacuum Atmospheres Model HE-93B), under nitrogen by-pass, in sealed ampoules, or using a conventional vacuum line. The commercially available starting materials were usually purified by distillation, crystallization, or other appropriate means.

Molecular weights (MW) were determined in chloroform solutions using a Mechrolab Osmometer Model 302 at concentrations of 4-6 mg/ml. In the case of polymers standardization curves based on polystyrenes of molecular weights 3600, 8000, 20000 and 49000 were employed. Infrared spectra were recorded on double mulls (Kel-F oil No. 10 and Nujol) using a Perkin-Elmer Corporation Infrared Spectrophotometer Model 21. Differential scanning calorimetry (DSC), differential thermal (DTA) and thermogravimetric analyses (TGA) were performed using a duPont 951/990 Thermal Analyzer.

All materials synthesized were dried at $100^{\circ}C$ or higher in vacuo before physical and chemical characterizations unless their melting point was lower than this temperature. The melting points of the monomers were determined in nitrogen filled or evacuated sealed capillaries, melting points of the polymers were obtained using a Fisher-Johns apparatus. The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

4.1 INTERMEDIATE AND MONOMER SYNTHESES

The intermediates: 2-chloro-4,6-diphenyl-s-triazine, 2-azido-4,6-diphenyl-s-triazine, 2,4-dichloro-6-phenyl-s-triazine, 2,4-diazido-6-phenyl-s-triazine, trimethylsilyl azide, and diphenylphosphinyl azide as well as the monomers $(C_6H_5)_2C_3N_3N=P(C_6H_5)_2C_6H_4CH=CH_2$, and $(C_6H_5)C_3N_3[N=P(C_6H_5)_2C_6H_4CH=CH_2]_2$ were synthesized using the procedures developed under the preceding program. (1)

The method previously employed for the preparation of diphenyl-p-styrylphosphine was simplified and the product could be prepared in good yield in the absence of the polymerization inhibitor. The procedure is given below:

Preparation of Diphenyl-p-styrylphosphine. In a 500 ml round bottom flask equipped with stirrer, reflux condenser, thermometer, and nitrogen by-pass were placed 17.74 g (0.741 mol) of magnesium turnings in a dry nitrogen atmosphere. To this were added 2.7 ml of ethyl bromide dissolved in 10 ml of dry tetrahydrofuran at 31-53°C over a period of 15 min. After stirring for an additional hr and subsequent cooling to 5°C, 50 g of p-chlorostyrene, dissolved in 80 ml of dry tetrahydrofuran were added over a period of 70 min with ice cooling at such a rate that the temperature of the solution never exceeded 23°C. The mixture then was stirred for 1.5 hr at room temperature before being transferred into a dropping funnel inside an inert atmosphere enclosure. This solution then was added in a nitrogen atmosphere to 67.9 g diphenylchlorophosphine dissolved in 250 ml dry tetrahydrofuran at 6-9°C over a 30 min period. The reaction mixture was subsequently stirred at room temperature for 1 hr, cooled to 6°C, and hydrolyzed by adding a solution of 72.5 g ammonium chloride in 500 ml of de-aerated water. After separating the organic layer from the aqueous

phase and washing the latter with two 250 ml portions of tetra-
hydrofuran the combined organic solutions were dried over sodium
sulfate overnight. After filtration the volume of the solution
was reduced to 50% by evaporating the solvent, whereupon
heptane was added to precipitate any polymer present. Since
no precipitate formed the solution was evaporated to dryness
and the remaining viscous oil treated in a nitrogen atmosphere
with boiling ethanol. In this manner 30.2 g (34%) of ethanol
insoluble material (probably polymer) were obtained whereas
from the ethanolic filtrate, after addition of water and cooling,
51.2 g (57.7%) of diphenyl-p-styrylphosphine, mp 77-78°C,
were isolated.

Attempted Preparation of $(C_6H_5)_2P(O)N=P(C_6H_5)_2C_6H_4CH=CH_2$. In an inert

atmosphere enclosure to a stirred solution of diphenyl-p-styryl-
phosphine (1.0 g, 3.468 mmol) and 4-t-butylpyrocatechol, a
polymerization inhibitor, (0.2 g) in tetrahydrofuran (20 ml) was
added diphenylphosphinyl azide (0.84 g, 3.468 mmol) in tetra-
hydrofuran (20 ml) over a period of 1 hr. Nitrogen evolution was
observed. Stirring at room temperature was continued for a total
of 14 days; since the disappearance of the azido group, as
evidenced by infrared spectroscopy, proceeded very slowly. After
removal of the solvent, a gummy product indicating the presence
of polymeric material, was obtained. The attempted isolation of the
monomeric product $(C_6H_5)_2P(O)N=P(C_6H_5)_2C_6H_4CH=CH_2$ was
unsuccessful.

Preparation of $(C_6H_5O)_2P(O)N=P(C_6H_5)_2C_6H_4CH=CH_2$

In an inert atmosphere enclosure to a stirred solution of diphenyl-p-
styrylphosphine (10.0 g, 34.68 mmol) and 4-t-butylpyrocatechol, a
polymerization inhibitor, (0.2 g) in tetrahydrofuran (100 ml) was

added a solution of diphenylphosphoryl azide (9.54 g, 34.66 mmol)
(which was obtained from Willow Brook Labs., Inc., Waukesha,
Wisconsin, and used as received), in tetrahydrofuran (100 ml)
over a period of 3 hr; immediate evolution of gas was observed.
The solution was then stirred at room temperature for 120 hr.
Subsequently the solvent was removed in vacuo; crystallization
from benzene-heptane gave 14.35 g of product (77.3% yield),
mp 150-152°C. Anal. calcd for $C_{32}H_{27}P_2NO_3$: C, 71.77%;
H, 5.08%; P, 11.57%; N, 2.62%; O, 8.96%; MW 535.53
Found: C, 71.87; H, 5.35; P, 11.51; N, 2.60, MW 569·

4.2   POLYMER SYNTHESES

The polymerizations were performed: (a) in solution
(this applied only to ionic polymerizations which were conducted
on styrene to determine the applicability of this procedure to
diphenyl-p-styrylphosphine systems), (b) in bulk using either a
sealed tube method or vacuum line pumping procedure.

The copolymers of the variously substituted ("oxidized")
diphenyl-p-styrylphosphines were prepared either by bulk co-
polymerizations of the actual monomers or by the reaction of the
preformed diphenyl-p-styrylphosphine polymer with the selected
azides and/or diazides.

4.2.1   Ionic Polymerizations

In a typical polymerization employing the $TiCl_4/(C_2H_5)_3Al$
catalyst system to a given volume of benzene (20-40 ml) was
added in an inert atmosphere, $TiCl_4$ (0.76-0.19 g) followed by
$(C_2H_5)_3Al$ (0.23-0.56 g). Subsequently to the black-brown stirred
mixture was added freshly distilled styrene ($\sim$4.0 g). In some
instances the reaction solution was heated, in others it was
stirred at room temperature. The reaction was terminated by

addition at 0°C of ethanol ($\sim$ 10 ml) followed by pouring the mixture into 200 ml of ethanol. To decolorize the dark solution usually 10 ml of 30% H_2O_2 was added at this point. The precipitated polymer was filtered and dried.

In the polymerization utilizing the $TiCl_4/C_4H_9Li$ catalyst system the reaction was carried out in hexane-heptane mixture. To the stirred heptane-$TiCl_4$ mixture the butyl lithium in hexane had to be added slowly to avoid vigorous reaction. The workup was basically the same as that delineated above except instead of ethanol, methanol was employed and the precipitated polymer was decolorized by washing with methanolic hydrogen chloride instead of the hydrogen peroxide treatment. The experiments performed are summarized in Table I.

4.2.2   Bulk Polymerizations

Two procedures were employed here: (a) the required quantity of the monomer or monomers (ca 2 g) was sealed in an evacuated glass ampoule which was then inserted for a specified period of time into an oven preheated to a predetermined temperature. Subsequently the ampoule was cooled to room temperature and opened. The product, if soluble, was then dissolved in chloroform ($\sim$ 10 ml) and the polymer was precipitated by pouring onto heptane ($\sim$ 200 ml), filtered and dried. (b) The required quantity of the monomer or monomers was placed in an ampoule which was then evacuated using the vacuum line. Once good vacuum (10^{-3} mm) was attained the ampoule was inserted into an oil bath preheated to predetermined temperature for a specified period of time. The workup was analogous to that delineated under (a). These investigations are summarized in Tables II to V.

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### 4.2.3   Solution Substitution of Preformed Polydiphenyl-p-styrylphosphine

This procedure was employed for the synthesis of substituted ("oxidized") homopolymers and copolymers. The three examples described below illustrate this technique. The polymers prepared by this method are listed in Table III.

a) __Preparation of__

$$\left[(C_6H_5O)_2P(O)N=P(C_6H_5)_2C_6H_4CH-CH_2\right]_x$$
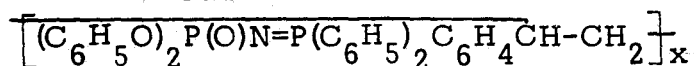
In an inert atmosphere enclosure to a stirred solution of polydiphenyl-p-styrylphosphine (2.00 g, 6.936 mmol) in tetrahydrofuran (40 ml) was added diphenylphosphoryl azide (1.91 g, 6.934 mmol) in tetrahydrofuran (40 ml) over a period of 1 hr; immediate gas evolution was observed. The solution was then stirred overnight at room temperature. Subsequently, the polymer was precipitated out with heptane (250 ml), filtered and dried in vacuo for 7 hr at 103°C affording 3.31 g (89% yield) of product, mp 142-166°C; MW > 50000. The TGA of this material is given in Fig. 21.

b) __Preparation of__

$$\left[\Phi_2P(O)N=P\Phi_2\Phi CH-CH_2\right]_{19.07x}\left[\Phi_2C_3N_3N=P\Phi_2\Phi CH-CH_2\right]_{1.00x}$$
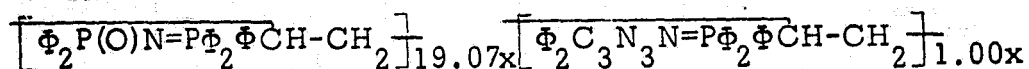
In an inert atmosphere enclosure to polydiphenyl-p-styrylphosphine (9.50 g, 32.95 mmol) in tetrahydrofuran (180 ml) was added diphenylphosphinyl azide (7.61 g, 31.29 mmol) in tetrahydrofuran (45 ml). The resulting solution was stirred at room temperature for 8 days. Subsequently to the solution was added 2-azido-4,6-diphenyl-s-triazine (0.45 g, 1.64 mmol). After stirring at room temperature for 24 hr the solution was poured onto heptane (500 ml). The precipitated product was filtered and dried in vacuo at 122-155°C for 10 hr giving 15.52 g (93% yield) of

33

polymer, mp 198-222°C; MW 54600. The TGA is given in Fig. 22;
the material is listed in Table VIII and its elemental composition
is presented in Table VII.

c) <u>Preparation of Candidate Terpolymer (Material F, Table VIII)</u>

In an inert atmosphere enclosure to polydiphenyl-p-styryl-
phosphine (2.00 g, 6.936 mmol) in tetrahydrofuran (20 ml) was
added diphenylphosphoryl azide (1.527 g, 5.549 mmol) in tetra-
hydrofuran (20 ml). The resulting solution was stirred at room
temperature for 5 days. Then to the solution was added 2-azido-
4,6-diphenyl-s-triazine (190 mg, 0.694 mmol) after 2 hr this
was followed by 2,4-diazido-6-phenyl-s-triazine (41.3 mg,
0.173 mmol). Subsequently after stirring for 14 hr at room
temperature an additional quantity of 2-azido-4,6-diphenyl-s-triazine
(95.0 mg, 0.347 mmol) was introduced. The resulting solution, fol-
lowing stirring at room temperature for 6 hr, was poured onto heptane
(200 ml). The precipitated product was filtered and dried in vacuo
at 90-93°C for 9 hr giving 3.39 g (93% yield) of polymer, mp
153-170°C; MW 91300. The TGA is given in Fig. 26; the material
is listed in Table VIII and its elemental composition is presented
in Table VI.

5. SUMMARY AND RECOMMENDATIONS

The objective of this program was the development of practical flame resistant polymeric compositions, which are amenable to fabrication and which do not form toxic or corrosive products upon oxidative thermal decomposition.

The feasibility of this undertaking was proven under a previous contract during which several materials were developed all of which were based on substituted diphenyl-p-styrylphosphine. The relatively low molecular weights of the polymers initially obtained necessitated the investigation of alternate or modified polymerization techniques. Furthermore, the poor processing characteristics of the products made it of importance to study the introduction of substituents promoting an internal plasticizing action.

The work performed under this contract resulted in the development of two polymerization methods, monomer bulk polymerization and substitution of preformed poly(diphenyl-p-styrylphosphine), which afforded a series of homo-, co-, and terpolymers. In addition, a novel monomer derived from a commercially available and thus relatively inexpensive intermediate, diphenylphosphoryl azide, was synthesized and incorporated into a variety of polymeric compositions. This substituent rendered the polymers more amenable to production of well adhering homogeneous films; however, its presence affected adversely the melting characteristics of the resultant materials. Tailoring the properties of the final product by using a carefully selected proportion of the various monomers in a terpolymer system appears to alleviate this deficiency. This approach has been explored

only to a limited extent under the current program, yet the results obtained to date show definite promise. The preliminary terpolymers synthesized exhibit definite enhancement of the desired characteristics such as, e.g., the melting behavior, without detrimental effect upon, i.e., the film forming capability. Such polymerization followed by solution crosslinking appears to present the best method for attaining high molecular weight practical compositions of the desired physical characteristics.

Under the previous contract the nontoxic nature of the thermal oxidative degradation products was determined by chemical analytical techniques. Under the current program three representative polymer systems were fabricated into washers and submitted for toxicological testing to NASA L. B. Johnson Space Center. No mortalities were recorded using maximum sample sizes permitted by the available instrumentation.

To summarize, in view of the proven nontoxic nature of the oxidative decomposition products formed by the polymeric compositions derived from the variously substituted diphenyl-p-styrylphosphines, the flame retardancy of these compositions, the ability of the phosphorus containing monomers to copolymerize with commercially used monomers, and the promising characteristics of the terpolymers developed thus far, it seems warranted to pursue further the modification and optimization of this type of compositions.

6. REFERENCES

1   K. L. Paciorek, D. W. Karle, and R. H. Kratzer,
        Final Report "Flame Resistant Nontoxic Polymer
        Development", Contract No. NAS9-12432,
        February 1973

2   G. Natta, et al, U. S. Patent 3 161 624 (1964)

3   K. C. Tsou, U. S. Patent 3 069 407 (1962)

4   E. M. Kuhn, U. S. Patent 3 040 013 (1962)

5   W. E. Gibbs, private communication

7. TABLES AND FIGURES

TABLE I

SUMMARY OF IONIC POLYMERIZATIONS

PERFORMED ON STYRENE[a]

Run No.	Styrene		Solvent	Catalyst				Condition		Polymer		
				TiCl$_4$		AlEt$_3$						
	g	mmol	ml	mg	mmol	mg	mmol	Temp °C	Time h	Yield %	MP °C	MW
1	4.16	39.95	40	760	4.01	460	4.03	RT[b]	72	10	108–123	6840
2	4.40	42.25	25	190	1.00	230	2.10	RT	64	15.5	nd[c]	nd
3	4.16	39.95	30	190	1.00	230	2.10	39–53 62–72	6 8	5.2	nd	nd
4[d]	9.07	87.09	20	949	5.00	–	–	RT	23	22.2	127–167	insol.[e]
5	4.16	39.95	15	760	4.01	450	4.03	RT	23	19	92–105[f] 130–153[f]	nd nd

a All the polymerizations with the exception of No. 4 were conducted in benzene.

b Room temperature.

c Not determined.

d This polymerization was performed using the catalytic system titanium tetrachloride and n-butyllithium; the butyl lithium used was 20.9% in hexane; 6.2 ml were employed; whereas the TiCl$_4$ was suspended in heptane.

e Molecular weight could not be determined since the material was only partially soluble in chloroform.

f It appeared that two different kinds of polymer were formed.

TABLE II

SUMMARY OF BULK POLYMERIZATIONS

CONDUCTED ON STYRENE[a]

Run No.	Monomer Amt g	Conditions		Polymer		
		Temp °C	Period h	Yield %	MP °C	MW
6	1.64	230	0.75	76	103–113	26000
12	2.43	230	1.5	70	97–108	14100
14	1.46	230	0.3	61	88–102	14800

a All the polymerizations were performed in sealed evacuated ampoules.

TABLE III

SUMMARY OF BULK POLYMERIZATIONS CONDUCTED
ON DIPHENYL-p-STYRYLPHOSPHINE [a]

Run No.	Monomer g		Conditions		Polymer		
			Temp °C	Period h	Yield %[b]	MP °C	MW
7	1.21	(I)[c]	230	0.75	69	140-165	67000
8	0.75	(II)	230	0.75	72	133-149	47000
10	0.76	(II)	230	1.5	80	130-140	28600
13	12.49	(II)	230	1.0	81	125-146	18000 ?
15	1.10	(II)	230	0.3	77	122-145	27000
17	12.15	(II)	230	0.75	87	127-140	31600
22	1.50	(II)	180	0.5	73	140-148	23300
18	2.00	(III)	210	0.5	77	126-135	16400
20	2.00	(III)	230	0.5	70	128-138	11100
19	2.00	(III)	250	0.5	58	120-136	9000
24	2.00	(IV)	100	24.0	6[d]	135-145	34000
26	2.00	(IV)	100	8.0	16[d]	125-135	12300
27	2.00	(IV)	100	1.0	23[e]	127-135	8700
28	2.00	(V)[f]	210	0.5	65	140-150	28200
29	2.00	(VI)	210	0.5	68	135-143	15200

a   All polymerizations were performed in evacuated ampoules either using sealed ampoules (Runs 7-17) or under pumping on vacuum line (Runs 18-29).

b   This is the yield of chloroform soluble polymer.

c   The Roman Numeral in the bracket denotes a specific batch of diphenyl-p-styrylphosphine.

d   The low yield of the chloroform soluble polymer is due to high gel formation.

e   The low yield obtained here is due to low conversion of the starting monomer.

f   This diphenyl-p-styrylphosphine was prepared in the absence of the polymerization inhibitor, 4-tert-butylpyrocatechol.

TABLE IV

SUMMARY OF BULK POLYMERIZATIONS CONDUCTED
ON PRE-OXIDIZED MONOMERS[a]

Run No.	Monomer Identification	Amt g	Temp °C	Period h	Yield %	MP °C	MW	TGA Fig. No.
11	$(\Phi O)_2 P(O)N=P\Phi_2\Phi CH=CH_2$	0.41	230	1.5	(90)[b]	108–125	n.a.[c]	–
25	$(\Phi O)_2 P(O)N=P\Phi_2\Phi CH=CH_2$	1.00	150	1.0	76	145–162	56300	–
30	$(\Phi O)_2 P(O)N=P\Phi_2\Phi CH=CH_2$	1.00	150	5.0	74	139–156	100000 +	5
31	$(\Phi O)_2 P(O)N=P\Phi_2\Phi CH=CH_2$	1.00	150	24	82	118–156	46200	–
35	$(\Phi O)_2 P(O)N=P\Phi_2\Phi CH=CH_2$	15.51	165	5.0	73 (13)	122–143 –	54500 –	6
32	$\Phi C_3 N_3[N=P\Phi_2\Phi CH=CH_2]_2$	1.00	130	5.0	n.r.[d]	n.a.	n.a.	–
33	$\Phi C_3 N_3[N=P\Phi_2\Phi CH=CH_2]_2$	1.00	160	5.0	16 (66)	195–214 > 295	– –	– 8
36	$\Phi_2 C_3 N_3 N=P\Phi_2\Phi CH=CH_2$	1.04	190	5.0	82	218–222	–	–
37	$\Phi_2 C_3 N_3 N=P\Phi_2\Phi CH=CH_2$	5.00	190	5.0	84	215–226	6600	–
38	$\Phi_2 C_3 N_3 N=P\Phi_2\Phi CH=CH_2$	2.04	230	0.75	90	225–240	10400	12
41	$\Phi_2 C_3 N_3 N=P\Phi_2\Phi CH=CH_2$	0.70	230	5.0	76	215–230	9500	–

a All polymerizations were in evacuated ampoules under pumping on vacuum line.

b The number in the bracket corresponds to the yield of chloroform insoluble polymer.

c Not applicable.

d No reaction.

TABLE V

SUMMARY OF BULK COPOLYMERIZATIONS AND TERPOLYMERIZATIONS[a]

Run No.	Monomer A Identification	Amt g	Monomer B Identification	Amt g	Monomer C Identification	Amt g	Mole Ratio A : B : C	Temp °C	Period h	Yield %	MP °C	MW	TGA Fig. No.
9	$\Phi_2P\Phi CH=CH_2$	0.75	$\Phi CH=CH_2$	0.36	n.a.[b]	n.a.	1.0 : 1.3	225	0.50	68	125–140	34000	–
16	$\Phi_2P\Phi CH=CH_2$	1.02	$\Phi CH=CH_2$	0.45	n.a.	n.a.	1.0 : 1.2	235	0.30	74	127–145	17000	–
34	$(\Phi O)_2P(O)N=P\Phi_2\Phi CH=CH_2$	2.00	$\Phi C_3N_3[N=P\Phi_2\Phi CH=CH_2]_2$	0.31	n.a.	n.a.	9.2 : 1.0	165	5.00	(82)[c] 4	> 295 92–100	n.d.[d] n.d.	13 –
39	$\Phi_2P\Phi CH=CH_2$	1.03	$\Phi_2C_3N_3N=P\Phi_2\Phi CH=CH_2$	2.00	n.a.	n.a.	1.0 : 1.0	230	0.75	80	194–204	15300	14
40	$\Phi_2C_3N_3N=P\Phi_2\Phi CH=CH_2$	2.07	$\Phi C_3N_3[N=P\Phi_2\Phi CH=CH_2]_2$	0.15	n.a.	n.a.	20.4 : 1.0	230	1.00	(48) 50	> 260 206–223	4300	16 15
44	$\Phi_2C_3N_3N=P\Phi_2\Phi CH=CH_2$	16.92	$\Phi C_3N_3[N=P\Phi_2\Phi CH=CH_2]_2$	1.23	n.a.	n.a.	19.6 : 1.0	230	2.0	(79) 14	240–270 187–200	3400	17 18
43	$(\Phi O)_2P(O)N=P\Phi_2\Phi CH=CH_2$	2.24	$\Phi_2C_3N_3N=P\Phi_2\Phi CH=CH_2$	0.74	$\Phi C_3N_3[N=P\Phi_2\Phi CH=CH_2]_2$	0.53	6.0 : 2.0 : 1.0	178	5.0	(86) 3	> 295 155–165	3900	19 –
46	$(\Phi O)_2P(O)N=P\Phi_2\Phi CH=CH_2$	2.00	$\Phi_2C_3N_3N=P\Phi_2\Phi CH=CH_2$	1.10	$\Phi C_3N_3[N=P\Phi_2\Phi CH=CH_2]_2$	0.17	6.0 : 3.3 : 0.35	173	5.0	(87) 5	> 295 115–130	4800	20 –

a   All polymerizations were performed in evacuated ampoules either using sealed ampoules (Runs 9,16) or under pumping on vacuum line (all the other runs).

b   Not applicable

c   The number in the bracket corresponds to the yield of chloroform insoluble polymer.

d   Not determined.

TABLE VI

ELEMENTAL ANALYSES DATA FOR REPRESENTATIVE POLYMERIC COMPOSITIONS

Polymer		Analyses %				
		C	H	P	N	O
$[(\Phi O)_2 P(O)N=P\Phi_2\Phi CH-CH_2]$ Run 30, Table IV	Calcd Found	71.77 71.77	5.08 5.36	11.57 11.73	2.62 2.79	8.96
$[\Phi_2 C_3 N_3 N=P\Phi_2\Phi CH-CH_2]$ Run 38, Table IV	Calcd Found	78.63 78.26	5.09 5.16	5.79 5.93	10.48 10.18	0.00
$[\Phi_2 P\Phi CH-CH_2]_{1.0}[\Phi CH-CH_2]_{1.3}$ Run 9, Table V	Calcd Found	86.16 85.75	6.52 6.36	7.32 8.08	0.00	0.00
$[\Phi_2 P\Phi CH-CH_2]_{1.0}[\Phi_2 C_3 N_3 N=P\Phi_2\Phi CH-CH_2]_{1.0}$ Run 39, Table V	Calcd Found	80.27 79.60	5.39 5.51	7.53 7.31	6.81 7.70	0.00
$[(\Phi O)_2 P(O)N=P\Phi_2\Phi CH-CH_2]_{8.00}[\Phi_2 C_3 N_3 N=P\Phi_2\Phi CH-CH_2]_{1.50}[\Phi C_3 N_3 (N=P\Phi_2\Phi CH-CH_2)_2]_{0.25}$ Run F, Table VIII	Calcd Found	73.03 71.27	5.09 5.23	10.56 10.69	4.06 4.36	7.26
$[(\Phi O)_2 P(O)N=P\Phi_2\Phi CH-CH_2]_{5.00}[\Phi_2 C_3 N_3 N=P\Phi_2\Phi CH-CH_2]_{4.00}[\Phi C_3 N_3 (N=P\Phi_2\Phi CH-CH_2)_2]_{0.35}$ Run H, Table VIII	Calcd Found	74.96 74.38	5.09 5.90	8.95 8.98	6.28 7.44	4.71

TABLE VII

CHARACTERIZATIONS OF POLYMERS SUBMITTED TO NASA L. B. JOHNSON

SPACE CENTER FOR TOXICOLOGY TESTING

Polymer Composition Identification	MP °C	MW Found	TGA Fig.		Analyses %				
					C	H	P	N	O
$[\Phi_2 P(O)N=P\Phi_2\Phi CH-CH_2]_{19.07x}[\Phi_2 C_3 N_3 N=P\Phi_2\Phi CH-CH_2]_{1.00x}$ 1-74-56-2 Run No. B, Table VIII	198-222	54600	22	Calcd Found	76.45 74.99	5.39 5.98	11.96 12.58	3.19 3.03	3.09
$[(\Phi O)_2 P(O)N=P\Phi_2\Phi CH-CH_2]_x$ 1-74-115-4 Run No. 35, Table IV	122-143	54500	6	Calcd Found	71.77 70.97	5.08 5.01	11.57 11.18	2.62 2.80	8.96
$[\Phi_2 C_3 N_3 N=P\Phi_2\Phi CH-CH_2]_{19.6x}[\Phi C_3 N_3 (N=P\Phi_2\Phi CH-CH_2)_2]_{1.00x}$ 1-74-137-3 Run No. 44, Table V	240-270	n.d.[a]	17	Calcd Found	78.56 76.17	5.10 4.99	5.95 5.74	10.39 9.82	0.00

a The molecular weight of this polymer could not be determined due to its insolubility in the solvents tried.

TABLE VIII

HOMOPOLYMERS, COPOLYMERS, AND TERPOLYMERS OBTAINED VIA "OXIDATION"
OF PREFORMED POLY(DIPHENYL-p-STYRYLPHOSPHINE)

No.	Composition	MP °C	MW	No. Units	TGA Fig.	Starting Material MW	No. Units
A	$[(\Phi O)_2 P(O)N=P\Phi_2\Phi CH-CH_2]_x$	142-166	>50000	93	21	11300	39
B	$[\Phi_2 P(O)N=P\Phi_2\Phi CH-CH_2]_{19.07x}[\Phi_2C_3N_3N=P\Phi_2\Phi CH-CH_2]_{1.00x}$	198-222	54600	102	22	18000	62
C	$[\Phi_2 P(O)N=P\Phi_2\Phi CH-CH_2]_{6.00x}[\Phi_2C_3N_3N=P\Phi_2\Phi CH-CH_2]_{2.00x}[\Phi C_3N_3(N=P\Phi_2\Phi CH-CH_2)_2]_{1.00x}$	240-282	n.d.[a]	-	23	31600	110
D	$[\Phi_2 P(O)N=P\Phi_2\Phi CH-CH_2]_{8.00x}[\Phi_2C_3N_3N=P\Phi_2\Phi CH-CH_2]_{1.50x}[\Phi C_3N_3(N=P\Phi_2\Phi CH-CH_2)_2]_{0.25x}$	205-220	23500	46	24	31600	110
E	$[(\Phi O)_2 P(O)N=P\Phi_2\Phi CH-CH_2]_{6.00x}[\Phi_2C_3N_3N=P\Phi_2\Phi CH-CH_2]_{2.00x}[\Phi C_3N_3(N=P\Phi_2\Phi CH-CH_2)_2]_{1.00x}$	202-215	n.d.	-	25	31600	110
F	$[(\Phi O)_2 P(O)N=P\Phi_2\Phi CH-CH_2]_{8.00x}[\Phi_2C_3N_3N=P\Phi_2\Phi CH-CH_2]_{1.50x}[\Phi C_3N_3(N=P\Phi_2\Phi CH-CH_2)_2]_{0.25x}$	153-170	91300	171	26	31600	110
G	$[(\Phi O)_2 P(O)N=P\Phi_2\Phi CH-CH_2]_{6.00x}[\Phi_2C_3N_3N=P\Phi_2\Phi CH-CH_2]_{3.50x}[\Phi C_3N_3(N=P\Phi_2\Phi CH-CH_2)_2]_{0.25x}$	170-180	25800	48	27	15000	52
H	$[(\Phi O)_2 P(O)N=P\Phi_2\Phi CH-CH_2]_{5.00x}[\Phi_2C_3N_3N=P\Phi_2\Phi CH-CH_2]_{4.00x}[\Phi C_3N_3(N=P\Phi_2\Phi CH-CH_2)_2]_{0.35x}$	170-192	38000	71	28	16000	55
I	$[(\Phi O)_2 P(O)N=P\Phi_2\Phi CH-CH_2]_{6.00x}[\Phi_2C_3N_3N=P\Phi_2\Phi CH-CH_2]_{3.30x}[\Phi C_3N_3(N=P\Phi_2\Phi CH-CH_2)_2]_{0.35x}$	170-215	46600	87	29	25750	89

a The molecular weight of this polymer could not be determined due to its insolubility in the solvents tried.

TABLE IX

SUMMARY OF MOLDING EXPERIMENTS[a]

Material Identification	Molding Conditions						Remarks
	Temp °F	Contact[b] Time min	Initial Load		Final Load		
			lbs	Time min	lbs	Time min	
[φ2P(O)N=Pφ2+CH-CH2]19.07x[φ2C3N3N=Pφ2+CH-CH2]1.00x[c] 1-74-56-2 (Run No. 8, Table VIII)	340	10	500	1	1000	4	Very good washers
[(φO)2P(O)N=Pφ2+CH-CH2]x[c] 1-74-115-4 (Run No. 35, Table IV)	260	10	500	1	1000	4	Very good washers
[φ2C3N3N=Pφ2+CH-CH2]19.6x[+C3N3(N=Pφ2+CH-CH2)2]1.00x[c] 1-74-137-3 (Insoluble, Run No. 44, Table V)	440	5	500	5	-	-	Acceptable, but brittle washers
[(φO)2P(O)N=Pφ2+CH-CH2]x (Run No. A, Table VIII)	260	-	10000	0.5	-	-	Clear film[d]
[(φO)2P(O)N=Pφ2+CH-CH2]x (Run No. 30, Table IV)	270	10	1000	1	2000	4	Good washer
[+C3N3[N=Pφ2+CH-CH2]2]x (Insoluble, Run No. 33, Table IV	400	10	500	5			Opaque, brittle washer
[φ2C3N3N=Pφ2+CH-CH2]x (Run No. 38, Table IV)	400	5	400	5	-	-	No success[e]
" "	450	5	750	5			No success[e]
" "	420	10	1500	5			No success[e]
" "	440	5	750	5			No success[e]
" "	470	10	1500	5			No success[e]
[(φO)2P(O)N=Pφ2+CH-CH2]x[+C3N3[N=Pφ2+CH-CH2]2]y (Insoluble, Run No. 34, Table V)	360	10	500	5		·	Acceptable washer
[(φO)2P(O)N=Pφ2+CH-CH2]6.00x[φ2C3N3N=Pφ2+CH-CH2]2.00x	440	10	750	5			Very good clear washer
[+C3N3(N=Pφ2+CH-CH2)2]1.00x (Run No. E, Table VIII)	360	10	750	5			Very good clear washer

a All the molding experiments were performed using the apparatus shown in Figure 30, in conjunction with Carver Laboratory Press Model C. All polymers were ground in a mortar before they were placed into the mold.

b The pressure used here was just contact pressure, this operation was performed to bring the sample up to temperature.

c These are the materials submitted to L. B. Johnson Space Center for toxocological testing.

d In this instance no mold was used, the powdered sample was placed on aluminum plates and was pressed.

e No washer could be fabricated, if at all formed it broke on removal from the mold or shortly thereafter.

PART NO. 990088

DSC RUN NO. 85 DATE 23 April 75

T-AXIS	DTA-DSC	TGA	TMA	
				Baseline: 505

OPERATOR F.S.
SAMPLE $\phi_2 P\phi CH=CH_2$
no inhibitor

ATM N_2 @
FLOW RATE 50 ml/min

T-AXIS
SCALE, °C/in 50
PROG. RATE, °C/min 5
HEAT ✓ COOL ___ ISO ___
SHIFT, in 0

DTA-DSC
SCALE. °C/in ___
(mcal/sec)/in ___
WEIGHT, mg ___
REFERENCE empty pan
1.0 (mcal/sec)/in Red
0.2 (mcal/sec)/in Green

TGA
SCALE, mg/in ___
SUPPRESSION, mg ___
WEIGHT, mg ___
TIME CONST, sec ___
dY, (mg/min)/in ___

TMA
SCALE, mils/in ___
MODE ___
SAMPLE SIZE ___
LOAD, g ___
dY,[10X],(mils/min)/in ___

MEASURED VARIABLE

TEMPERATURE, °C (CHROMEL / ALUMEL)
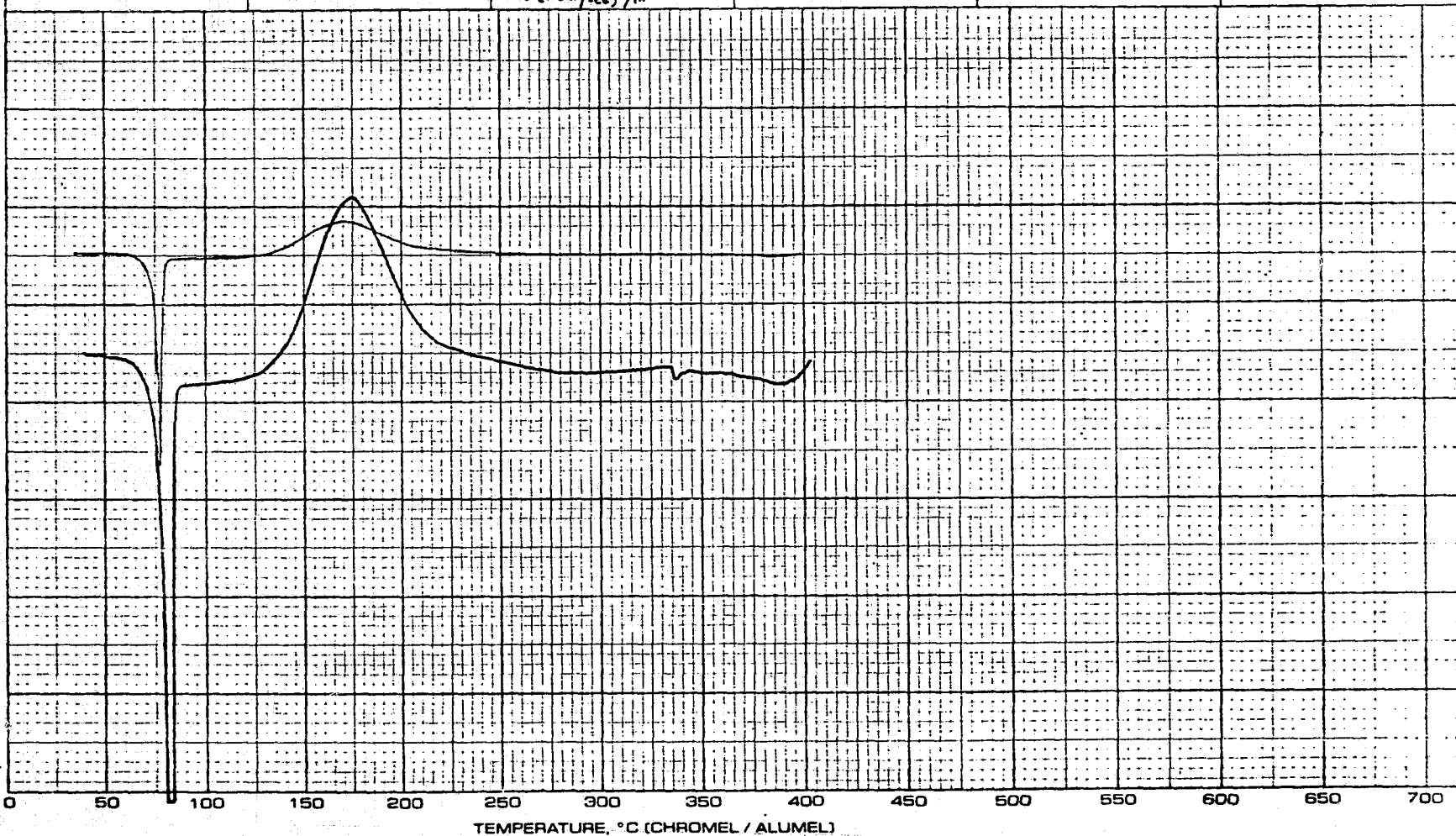
Figure 1:

DSC of $(C_6H_5)_2PC_6H_4CH=CH_2$

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PART NO. 990088

DSC RUN NO **86** DATE **24 April 75**	T-AXIS	DTA-DSC	TGA	TMA	Baseline: **505**
OPERATOR ___ **F.S.** ___ SAMPLE: **φ₂Pφ CH=CH₂** **no inhibitor** ATM ___ **N₂** ___ @ ___ FLOW RATE ___ **50 ml/min**	SCALE, °C/in ___ **50** ___ PROG. RATE, °C/min ___ **5** ___ HEAT ___✓___ COOL ___ ISO ___ SHIFT, in ___ **0** ___	SCALE, °C/in ___ ___ (mcal/sec)/in ___ WEIGHT, mg ___ REFERENCE ___ **empty pan** ___ **1.0** (mcal/sec)/in ___ **Red** **0.2** (mcal/sec)/in ___ **Green**	SCALE, mg/in ___ SUPPRESSION, mg ___ WEIGHT, mg ___ TIME CONST., sec ___ dY, (mg/min)/in ___	SCALE, mils/in ___ MODE ___ SAMPLE SIZE ___ LOAD, g ___ dY,(10X),(mils/min)/in ___	

DUPONT Instruments

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MEASURED VARIABLE

TEMPERATURE, °C (CHROMEL / ALUMEL)

Figure 2:

DSC of $(C_6H_5)_2PC_6H_4CH=CH_2$

PART NO. 990086

DSC

RUN NO **87** DATE **24 April 75**

OPERATOR **F.S.**

SAMPLE **Re-run of sample from DSC #86** (φ₂PφCH=CH₂ previously heated to 200°C)

SAMPLE Re-run of sample from DSC #86 ($\phi_2P\phi CH=CH_2$ previously heated to 200°C)

ATM **N₂** @

FLOW RATE **50 ml/min**

T-AXIS
SCALE, °C/in **50**

PROG. RATE, °C/min **5**

HEAT **✓** COOL ___ ISO ___

SHIFT, in **0**

DTA-DSC
SCALE, °C/in ___

(mcal/sec)/in ___

WEIGHT, mg ___

REFERENCE **empty pan**

1.0 (mcal/sec)/in **Red**

0.2 (mcal/sec)/in **Green**

TGA
SCALE, mg/in ___

SUPPRESSION, mg ___

WEIGHT, mg ___

TIME CONST., sec ___

dY, (mg/min)/in ___

TMA
SCALE, mils/in ___

MODE ___

SAMPLE SIZE ___

LOAD, g ___

dY, (10X), (mils/min)/in ___

Baseline: 505

MEASURED VARIABLE

50

TEMPERATURE, °C (CHROMEL / ALUMEL)
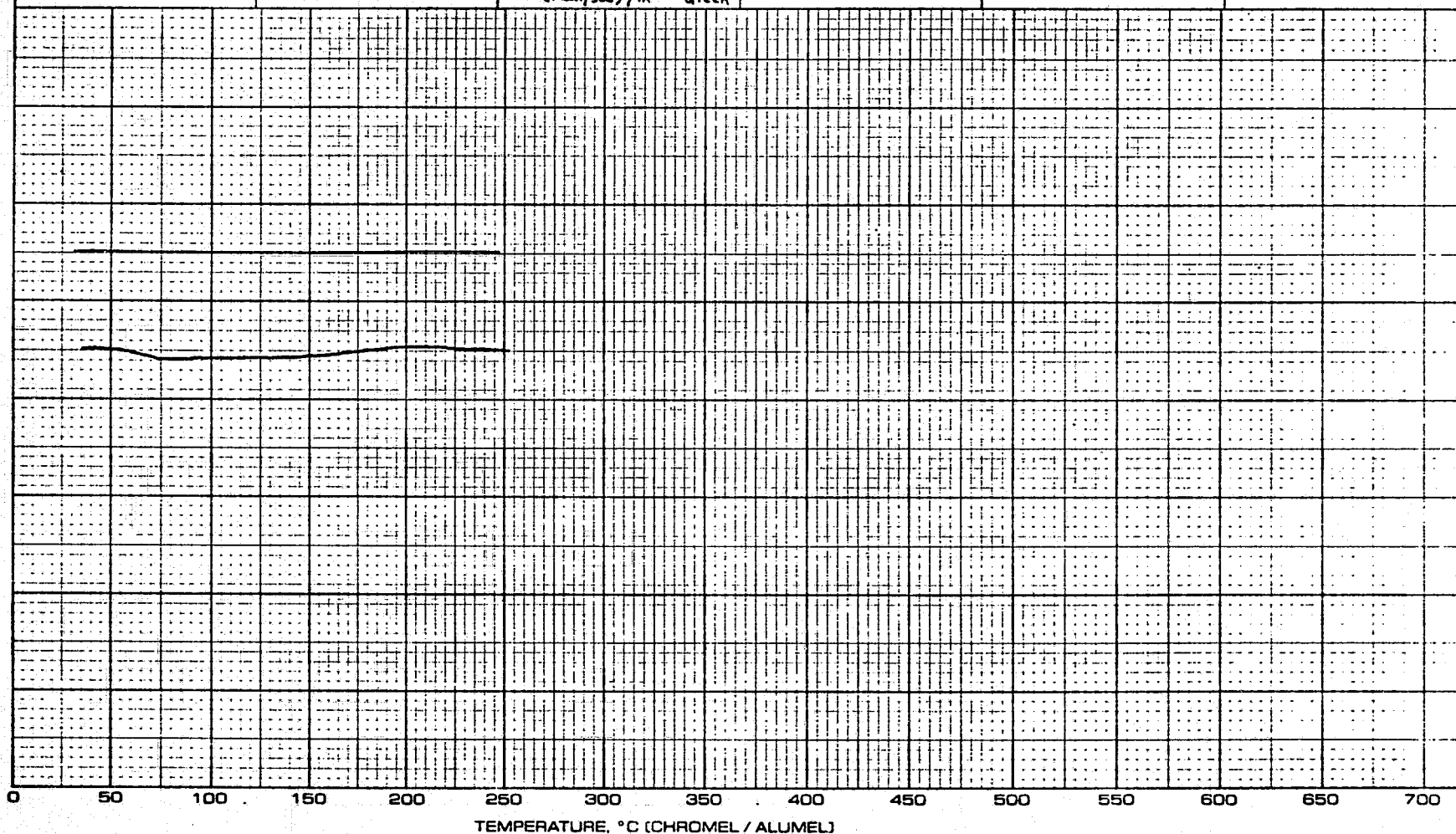
Figure 3:

DSC of $(C_6H_5)_2PC_6H_4CH=CH_2$ after heating to 200°C
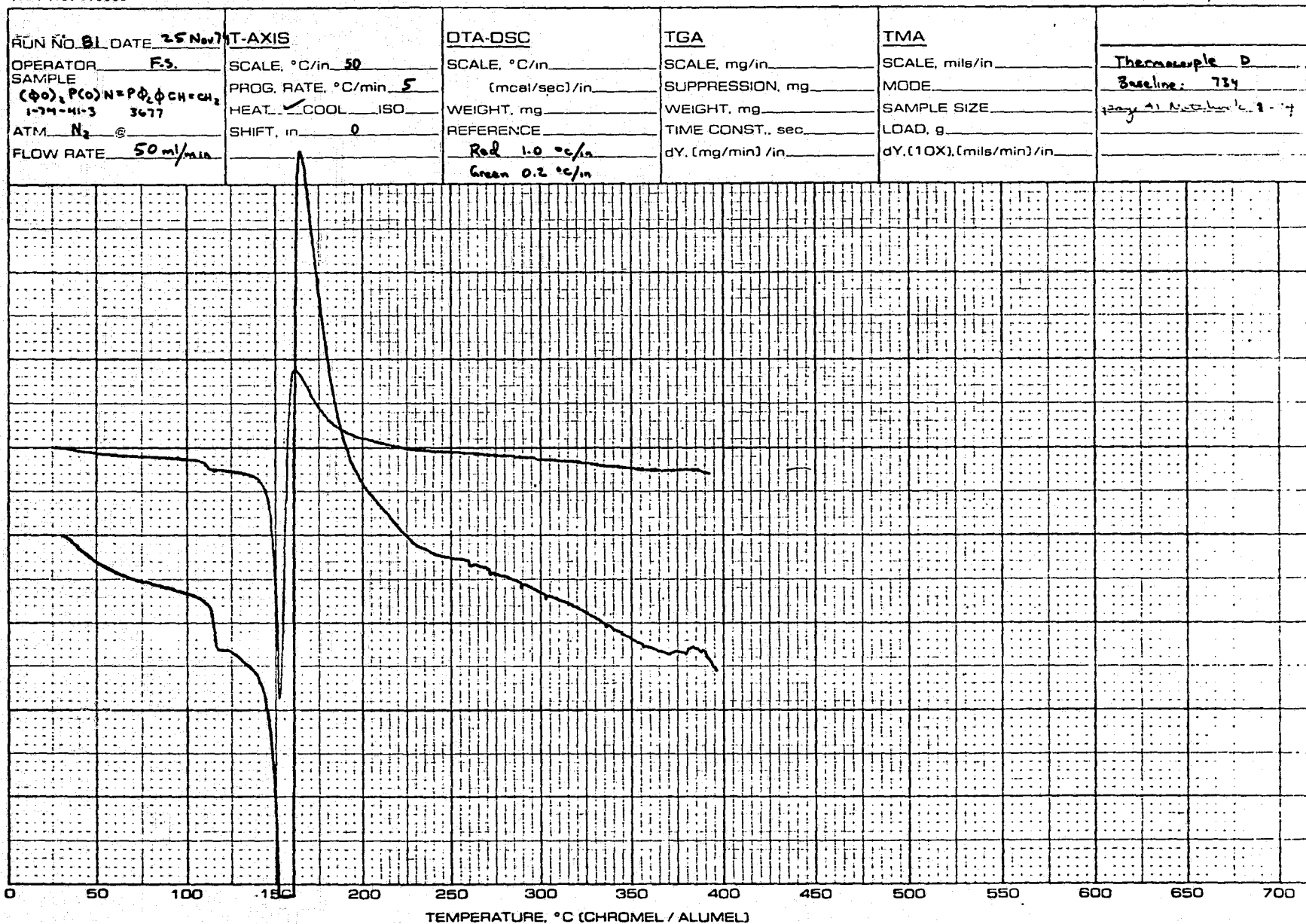
Figure 4:

DSC of $(C_6H_5O)_2P(O)N=P(C_6H_5)_2C_6H_4CH=CH_2$

PART NO. 990088

TGA RUN NO 178 DATE 6 SEPT 74

OPERATOR W
SAMPLE 1-74-102-2

150° 5 hrs
ATM AIR %
FLOW RATE 12 ml/min

T-AXIS
SCALE. °C/in 50
PROG. RATE. °C/min 5
HEAT ✓ COOL ___ ISO
SHIFT. in 0

DTA-DSC
SCALE. °C/in ___
(mcal/sec)/in ___
WEIGHT. mg ___
REFERENCE ___

TGA
SCALE. mg/in 1.0
SUPPRESSION. mg 0(20)
WEIGHT. mg 10.44
TIME CONST., sec 1
dY. (mg/min)/in 0.2

TMA
SCALE. mils/in ___
MODE ___
SAMPLE SIZE ___
LOAD. g ___
dY.(10X),(mils/min)/in ___

MEASURED VARIABLE

52

TEMPERATURE, °C (CHROMEL / ALUMEL)

Figure 5:

TGA of $\left[(C_6H_5O)_2P(O)N=P(C_6H_5)_2C_6H_4CH-CH_2 \right]_x$

Run 30, Table IV

TGA

RUN NO. 240 DATE 1 April 75

OPERATOR F.S.

SAMPLE 1-74-116-4 IR # 4078

[(ΦO)₂P(O)N=PΦ₂C₆H₄CHCH₂]ₓ
polymer 160°C, 5 hrs
large batch

ATM Air @

FLOW RATE 67 ml/min

T-AXIS

SCALE, °C/in 50

PROG. RATE, °C/min 5

HEAT ✓ COOL ISO

SHIFT, in 0

DTA-DSC

SCALE, °C/in

(mcal/sec)/in

WEIGHT, mg

REFERENCE

TGA

SCALE, mg/in 1.0

SUPPRESSION, mg 0(2.0)

WEIGHT, mg 12.79

TIME CONST., sec 1

dY, (mg/min)/in 0.2

TMA

SCALE, mils/in

MODE

SAMPLE SIZE

LOAD, g

dY.(10X).(mils/min)/in

DUPONT Instruments

53

MEASURED VARIABLE

TEMPERATURE, °C (CHROMEL / ALUMEL)

Figure 6:

TGA of $\left[(C_6H_5O)_2P(O)N=P(C_6H_5)_2C_6H_4CH-CH_2\right]_x$

Run 35, Table IV

DSC.
RUN NO. 61 DATE 25 Sept 74
OPERATOR F.S.
SAMPLE 1-74-107-1
$\phi C_3 N_3 (N=P\phi_2 C_6 H_4 CH=CH_2)_2$
ATM N₂ @
FLOW RATE 50 ml/min

T-AXIS
SCALE, °C/in 50
PROG. RATE, °C/min 5
HEAT ✓ COOL ISO
SHIFT, in 0

DTA-DSC
SCALE, °C/in
(mcal/sec)/in
WEIGHT, mg
REFERENCE
Red 1.0 (mcal/sec)/in
Green 0.2 (mcal/sec)/in

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST., sec
dY, (mg/min)/in

TMA
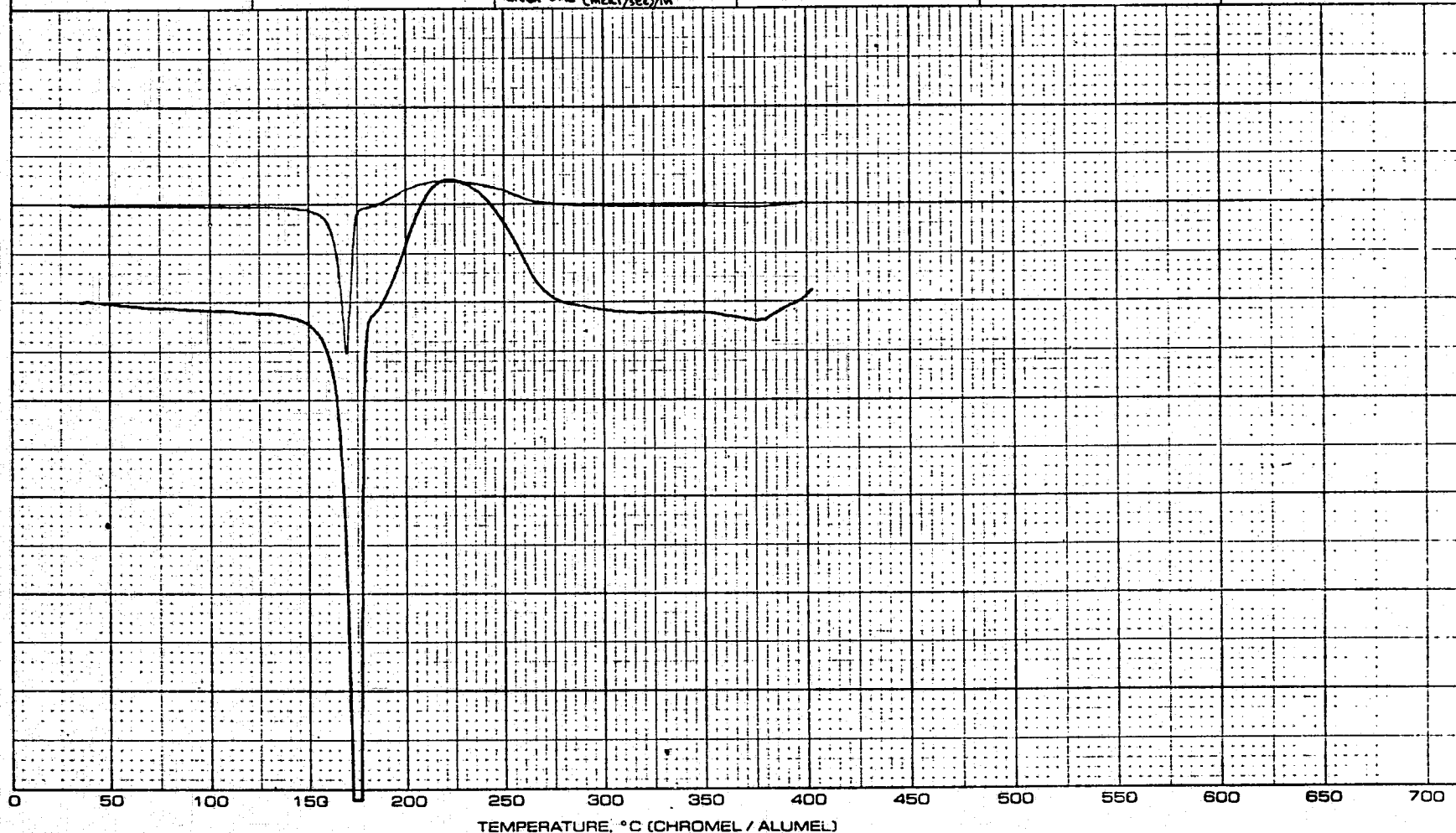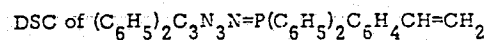SCALE, mils/in
MODE
SAMPLE SIZE
LOAD, g
dY,(10X),(mils/min)/in

Baseline Slope: 505

DUPONT Instruments

MEASURED VARIABLE

TEMPERATURE, °C (CHROMEL / ALUMEL)

Figure 7:

DSC of $C_6 H_5 C_3 N_3 [N=P(C_6 H_5)_2 C_6 H_4 CH=CH_2]_2$

TGA

RUN NO. 187 DATE 11 Oct 74

OPERATOR F.S.
SAMPLE 1-74-113-@
 TDA · 2DPPS 160°, 5 hrs.
 Insoluble
ATM Air @
FLOW RATE 67 ml/min

T-AXIS

SCALE, °C/in 50
PROG. RATE, °C/min 5
HEAT ✓ COOL ISO
SHIFT, in 0

DTA-DSC

SCALE, °C/in
(mcal/sec)/in
WEIGHT, mg
REFERENCE

TGA

SCALE, mg/in 1.0
SUPPRESSION, mg 0(20)
WEIGHT, mg 9.34
TIME CONST., sec 1
dY, (mg/min)/in 0.2

TMA

SCALE, mils/in
MODE
SAMPLE SIZE
LOAD, g
dY,(10X),(mils/min)/in

(DUPONT) Instruments

55

MEASURED VARIABLE

TEMPERATURE, °C (CHROMEL / ALUMEL)

Figure 8:

TGA of $\overline{[(C_6H_5)C_3N_3[N=P(C_6H_5)_2C_6H_4CH-CH_2]_2]_{\frac{1}{x}}}$
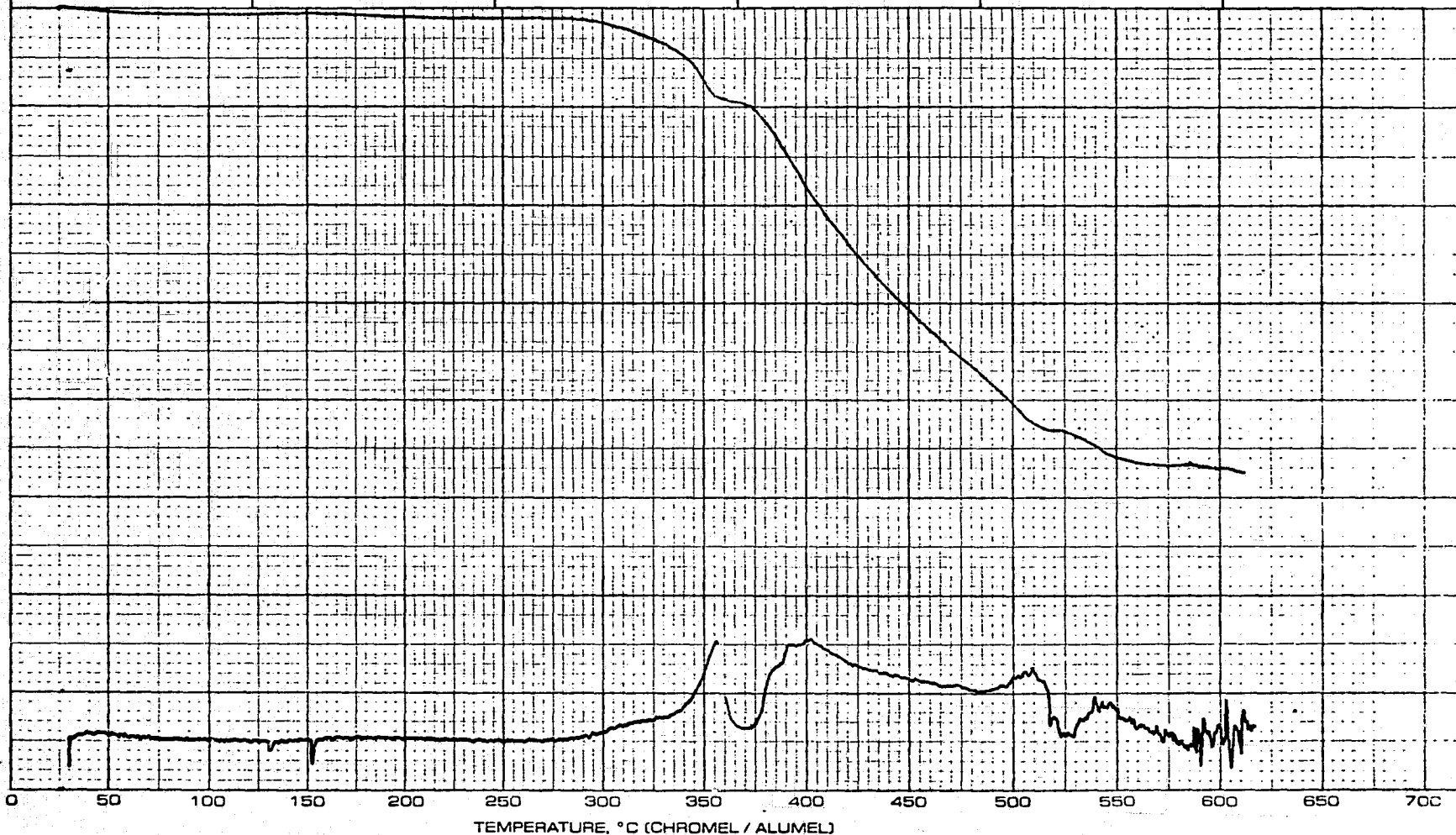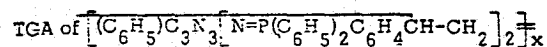
Run 33, Table IV

PART NO. 990088

DSC

RUN NO 88 DATE 8 May 75

OPERATOR F.S.

SAMPLE IR # 3740

$\Phi_2 C_3 N_3 N = P \Phi, C_6 H_4 CH = CH_2$
$C_6 H_6 / naptha$

ATM N_2 @

FLOW RATE 50 ml/min

T-AXIS

SCALE, °C/in 50

PROG. RATE, °C/min 5

HEAT ✓ COOL ISO

SHIFT, in 0

DTA-DSC

SCALE, °C/in

(mcal/sec)/in

WEIGHT, mg

REFERENCE empty pan

Red 1.0 (mcal/sec)/in

Green 0.2 (mcal/sec)/in

TGA

SCALE, mg/in

SUPPRESSION, mg

WEIGHT, mg

TIME CONST, sec

dY, (mg/min)/in

TMA

SCALE, mils/in

MODE

SAMPLE SIZE

LOAD, g

dY,(10X),(mils/min)/in

Baseline: 505

wt. of sample & capsule: 0.0662

wt. of capsule only: 0.0576

wt. of sample : 0.0086 g

MEASURED VARIABLE

TEMPERATURE, °C (CHROMEL / ALUMEL)

DUPONT Instruments

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Figure 9:

DSC of $(C_6H_5)_2C_3N_3N = P(C_6H_5)_2C_6H_4CH = CH_2$

PART NO. 990088

DSC

RUN NO. 66 DATE 9 Oct 74

OPERATOR F.S.
SAMPLE IR # 3790
$\phi_2 C_3 H_3 N = P\phi_2 \phi CH = CH_2$
$C_6 H_6 /$ Heptane
ATM N_2 @
FLOW RATE 50 ml/min

T-AXIS
SCALE, °C/in 50
PROG. RATE, °C/min 5
HEAT ✓ COOL ISO
SHIFT, in 0

DTA-DSC
SCALE, °C/in
[mcal/sec]/in
WEIGHT, mg 7.3
REFERENCE
Red 1.0 (mcal/sec)/in
Green 0.2 (mcal/sec)/in

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST., sec
dY, [mg/min] /in

TMA
SCALE, mils/in
MODE
SAMPLE SIZE
LOAD, g
dY,[10X],[mils/min]/in

Exc range 116 (pook 1-2
Baseline: 505
wt. of capsule: 0.0653
wt. of capsule: 0.0580 g
wt. of sample: 0.0073

MEASURED VARIABLE

57

TEMPERATURE, °C (CHROMEL / ALUMEL)

Figure 10:

DSC of $(C_6H_5)_2C_3N_3N = P(C_6H_5)_2C_6H_4CH = CH_2$

PART NO. 990088 *Note done on the same sample as 66*

DSC

RUN NO **67** DATE **9 Oct 74**
OPERATOR **F.S.**
SAMPLE IR # **5740** } report of DSC #66
$\Phi_2 C_3 N_3 N = P\Phi_2 \phi CH = CH_2$
C_6H_6 / Heptane
ATM **N_2** ε
FLOW RATE **50 ml/min**

T-AXIS
SCALE, °C/in **50**
PROG. RATE, °C/min **5**
HEAT ✓ COOL ___ ISO ___
SHIFT, in **0**

DTA-DSC
SCALE, °C/in ___
(mcal/sec)/in ___
WEIGHT, mg **7.2**
REFERENCE ___
Red: **1.0** (mcal/sec)/in
Green **0.1** (mcal/sec)/in

TGA
SCALE, mg/in ___
SUPPRESSION, mg ___
WEIGHT, mg ___
TIME CONST., sec ___
dY, (mg/min) /in ___

TMA
SCALE, mils/in ___
MODE ___
SAMPLE SIZE ___
LOAD, g ___
dY,(10X),(mils/min)/in ___

See page in book 1-74
Baseline: **505**
wt. after DSC # 66: **0.0652 g**
wt. capsule : **0.0532 g**
wt. sample : **0.0272 g**

charge upper limit to 400°C
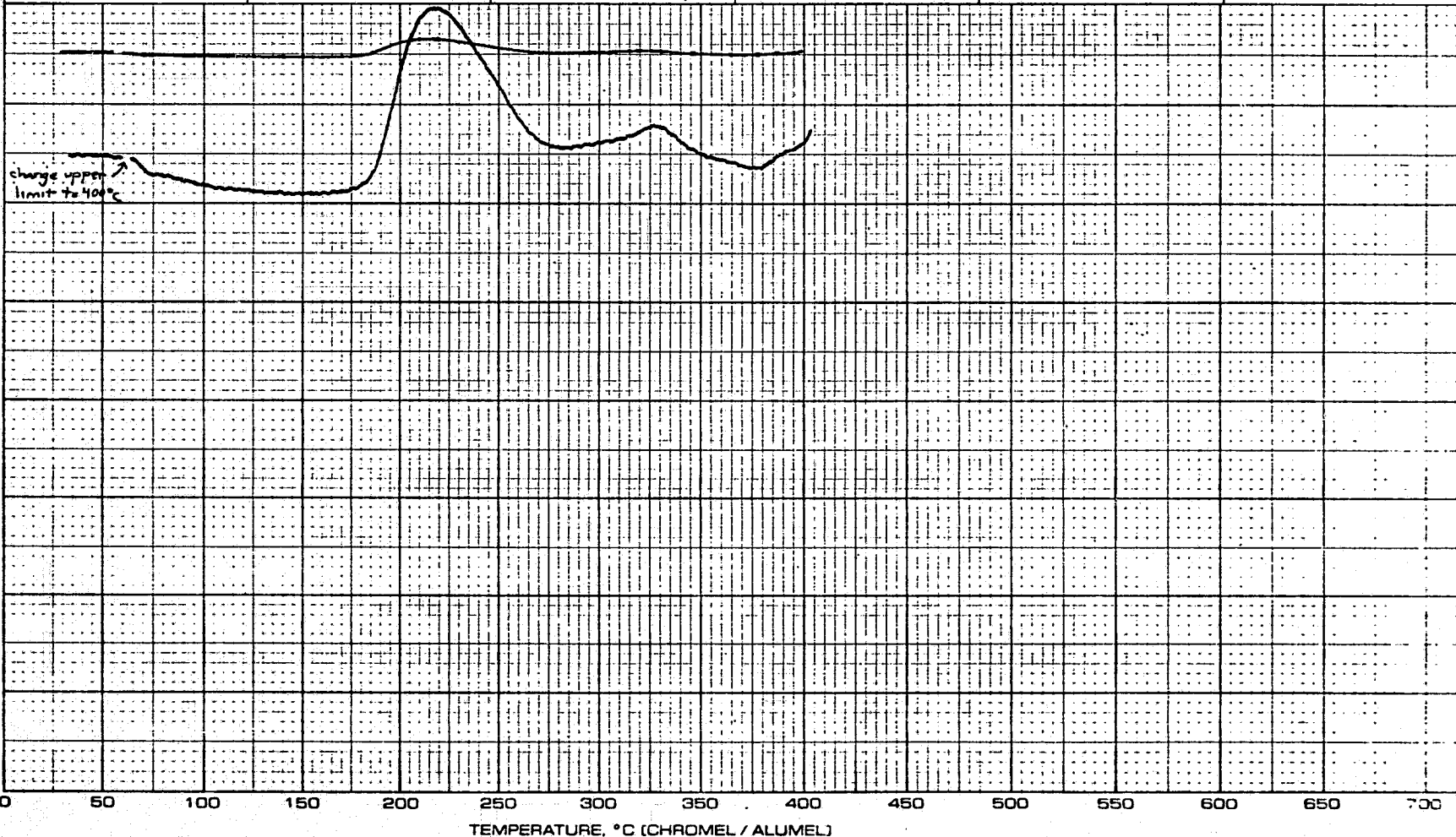
Figure 11:

DSC of $(C_6H_5)_2 C_3 N_3 N = P(C_6H_5)_2 C_6 H_4 CH = CH_2$ after heating to $200^\circ C$

TGA

RUN NO 250 DATE 29 April 75

OPERATOR F.S.

SAMPLE 1-74-121-2

$[\phi_2 C_3 N_3 N = P\phi_2 \phi CHCH_2]$

ATM Air @

FLOW RATE 67 ml/min

T-AXIS
SCALE, °C/in 50

PROG. RATE, °C/min 5

HEAT ✓ COOL ISO

SHIFT, in 0

DTA-DSC
SCALE, °C/in

(mcal/sec)/in

WEIGHT, mg

REFERENCE

TGA
SCALE, mg/in 1.0

SUPPRESSION, mg 0(20)

WEIGHT, mg 10.77

TIME CONST., sec 1

dY, (mg/min)/in 0.2

TMA
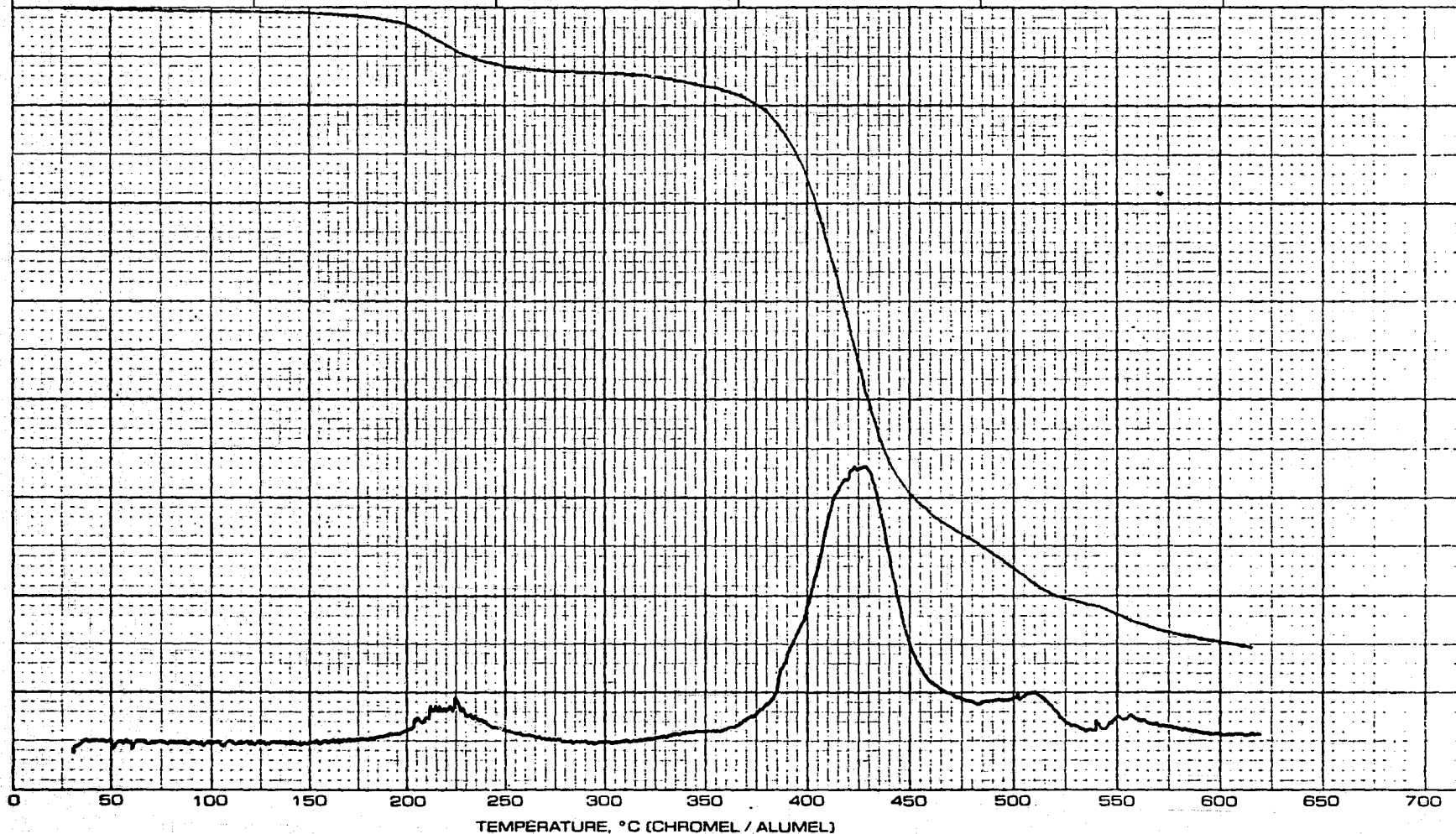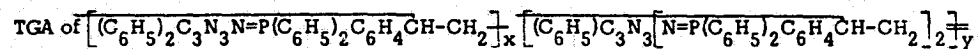SCALE, mils/in

MODE

SAMPLE SIZE

LOAD, g

dY,(10X),(mils/min)/in

(DUPONT) Instruments

MEASURED VARIABLE

59

TEMPERATURE, °C (CHROMEL / ALUMEL)

0   50   100   150   200   250   300   350   400   450   500   550   600   650   700

Figure 12:

TGA of $\left[(C_6H_5)_2C_3N_3N=P(C_6H_5)_2C_6H_4CH-CH_2\right]_x$

Run 38, Table IV

TGA

RUN NO 183 DATE 8 Oct 74

OPERATOR F.S.

SAMPLE 1-74-114-2
DPPOA · DPPS / TDA · 2DPPS

9/1 Insoluble

ATM Air @

FLOW RATE 67 ml/min

T-AXIS

SCALE, °C/in 50

PROG. RATE, °C/min 5

HEAT ✓ COOL ___ ISO

SHIFT, in 0

DTA-DSC

SCALE, °C/in _____

[mcal/sec]/in _____

WEIGHT, mg _____

REFERENCE _____

TGA

SCALE, mg/in 1

SUPPRESSION, mg (0)10

WEIGHT, mg 10.83

TIME CONST., sec 1

dY, (mg/min)/in _____

TMA

SCALE, mils/in _____

MODE _____

SAMPLE SIZE _____

LOAD, g _____

dY,(10X),(mils/min)/in _____

DUPONT Instruments

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MEASURED VARIABLE

TEMPERATURE, °C (CHROMEL / ALUMEL)

Figure 13:

TGA of $\left[(C_6H_5O)_2P(O)N=P(C_6H_5)_2C_6H_4CH-CH_2 \right]_{9.2x} \left[(C_6H_5)C_3N_3 \left[N=P(C_6H_5)_2C_6H_4CH-CH_2 \right]_2 \right]_{1.0x}$

Run 34, Table V

PART NO. 990088

TGA

RUN NO. 192 DATE. 4 Nov 74

	T-AXIS	DTA-DSC	TGA	TMA	
OPERATOR ___F.S___	SCALE, °C/in __50__	SCALE, °C/in ____	SCALE, mg/in ___1.0___	SCALE, mils/in ____	
SAMPLE ___1-74-122-2___	PROG RATE, °C/min __5__	(mcal/sec)/in ____	SUPPRESSION, mg __0(20)__	MODE ____	
COPOLYMER 1:1	HEAT __/__ COOL ___ISO___	WEIGHT, mg ____	WEIGHT, mg ___9.27___	SAMPLE SIZE ____	
$\phi_2C_3H_3N=P\phi_2C_6H_4CH_2/\phi\phi CH_2CH_2$					
ATM __Air__ @	SHIFT, in ___0___	REFERENCE ____	TIME CONST., sec __1__	LOAD, g ____	
FLOW RATE ___67ml/min___			dY, (mg/min)/in __0.2__	dY,(10X),(mils/min)/in ____	

MEASURED VARIABLE.

TEMPERATURE, °C (CHROMEL / ALUMEL)

Figure 14:

TGA of $\left[(C_6H_5)_2PC_6H_4CH-CH_2\right]_{1.0x}$ $\left[(C_6H_5)_2C_3N_3N=P(C_6H_5)_2C_6H_4CH-CH_2\right]_{1.0x}$

Run 39, Table V

TGA

RUN NO 197 DATE 15 Nov 74

OPERATOR ___F.S.___

SAMPLE φ₂C₃N₃N=Pφ₂φCH=CH₂
+C₃N₃[N=Pφ₂φCH=CH₂]
Copolymer − Soluble 1-74-12-4

ATM ___Air___ @

FLOW RATE ___67 ml/min___

T-AXIS

SCALE, °C/in ___50___

PROG. RATE, °C/min ___5___

HEAT ✓ COOL___ ISO___

SHIFT. in ___0___

DTA-DSC

SCALE, °C/in ___

(mcal/sec)/in ___

WEIGHT, mg ___

REFERENCE ___

TGA

SCALE, mg/in ___1.0___

SUPPRESSION, mg ___0(20)___

WEIGHT, mg ___10.87___

TIME CONST., sec ___1___

dY, (mg/min)/in ___0.2___

TMA

SCALE, mils/in ___

MODE ___

SAMPLE SIZE ___

LOAD, g ___

dY,(10X),(mils/min)/in ___

DU PONT Instruments

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MEASURED VARIABLE

TEMPERATURE, °C (CHROMEL / ALUMEL)

Figure 15:

TGA of $\left[(C_6H_5)_2C_3N_3N{=}P(C_6H_5)_2C_6H_4CH{-}CH_2\right]_x\left[(C_6H_5)C_3N_3\left[N{=}P(C_6H_5)_2C_6H_4CH{-}CH_2\right]_2\right]_y$

Soluble portion, Run 40, Table V

TGA

RUN NO. 199 DATE 20 Nov 74

OPERATOR W

SAMPLE 74-124-5 dried copolymer insoluble $\phi_2 C_3 N_3 N = P\phi_2 \phi CH = CH_2$ @ $\phi C_3 N_3 N = P\phi_2$

ATM AIR

FLOW RATE 67 ml/min

T-AXIS
SCALE, °C/in 50
PROG. RATE, °C/min 5
HEAT ✓ COOL ISO
SHIFT, in 0

DTA-DSC
SCALE, °C/in
(mcal/sec)/in
WEIGHT, mg
REFERENCE

TGA
SCALE, mg/in 1.0
SUPPRESSION, mg 0(20)
WEIGHT, mg 10.53
TIME CONST., sec 1
dY, (mg/min)/in 0.2

TMA
SCALE, mils/in
MODE
SAMPLE SIZE
LOAD, g
dY, (10X), (mils/min)/in

MEASURED VARIABLE

63

TEMPERATURE, °C (CHROMEL / ALUMEL)

Figure 16:

TGA of $\left[(C_6H_5)_2 C_3 N_3 N=P(C_6H_5)_2 C_6H_4 CH-CH_2\right]_x \left[(C_6H_5) C_3 N_3 \left[N=P(C_6H_5)_2 C_6H_4 CH-CH_2\right]_2\right]_y$

Insoluble portion, Run 40, Table V

PART NO. 990088

[φ₂C₃N₃N=Pφ₂φCH—CH₂]₉₅ₓ [φ₆₃N₃(N=Pφ₂φCH—CH₃)₂]₆ₓ

TGA

RUN NO. **203** DATE 5 Dec 74

OPERATOR _____ F.S.

SAMPLE TMA·DPPS / TDA·DPPS(5%)
230°C 2 hrs Insoluble
1-74-137-3

ATM _____ Air @

FLOW RATE 67 ml/min

T-AXIS

SCALE, °C/in 50

PROG. RATE, °C/min 5

HEAT ✓ COOL _____ ISO _____

SHIFT, in 0

DTA-DSC

SCALE, °C/in _____

(mcal/sec)/in _____

WEIGHT, mg _____

REFERENCE _____

TGA

SCALE, mg/in 1.0

SUPPRESSION, mg 0(20)

WEIGHT, mg 10.80

TIME CONST., sec 1.0

dY, (mg/min)/in 0.2

TMA

SCALE, mils/in _____

MODE _____

SAMPLE SIZE _____

LOAD, g _____

dY,(10X),(mils/min)/in _____

MEASURED VARIABLE

TEMPERATURE, °C (CHROMEL / ALUMEL)

Figure 17:

TGA of $\left[(C_6H_5)_2C_3N_3N=P(C_6H_5)_2C_6H_4CH-CH_2\right]_x\left[(C_6H_5)C_3N_3\left[N=P(C_6H_5)_2C_6H_4CH-CH_2\right]_2\right]_y$
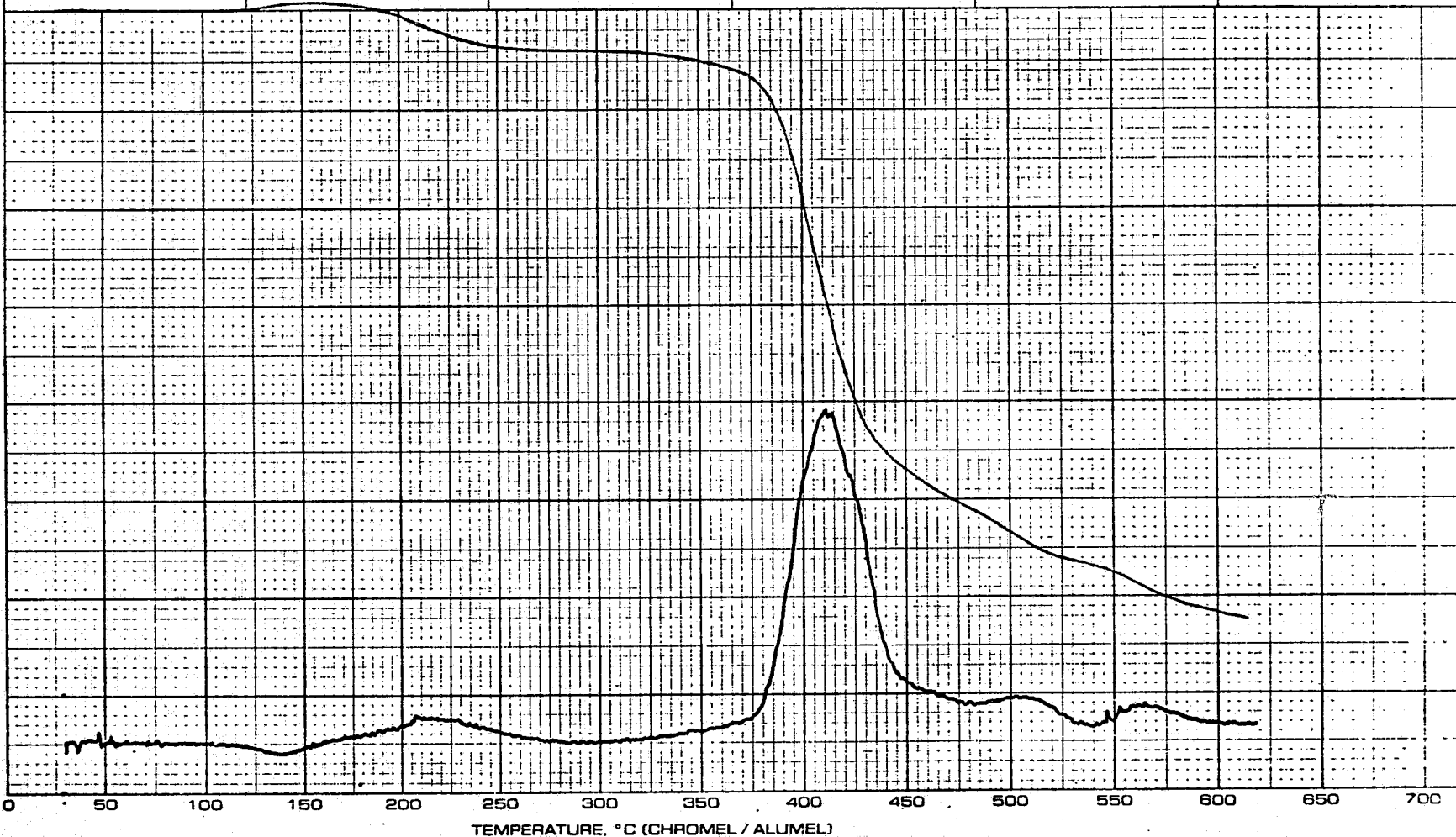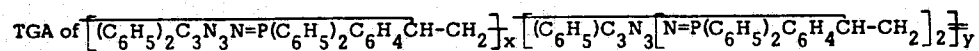
Insoluble portion, Run 44, Table V

PART NO. 990088

TGA

$\left[\text{...} \right]_{5x} \left[\text{...} \right]_{6x}$

RUN NO. 204 DATE 9 Dec 74

	T-AXIS	DTA-DSC	TGA	TMA	
OPERATOR F.S.	SCALE, °C/in 50	SCALE, °C/in	SCALE, mg/in 1.0	SCALE, mils/in	
SAMPLE Soluble TMA-DPPS/	PROG. RATE, °C/min 5	(mcal/sec)/in	SUPPRESSION, mg 0(20)	MODE	
TMA - ZDPPS (5%) Polymer	HEAT ✓ COOL ISO	WEIGHT, mg	WEIGHT, mg 11.00	SAMPLE SIZE	
1-74-137-4 230° 2 hrs	SHIFT, in 0	REFERENCE	TIME CONST., sec 1.0	LOAD, g	
ATM Air @			dY, (mg/min)/in 0.2	dY,(10X),(mils/min)/in	
FLOW RATE 67 ml/min					

DUPONT Instruments

MEASURED VARIABLE

TEMPERATURE, °C (CHROMEL / ALUMEL)

Figure 18:

TGA of $\left[(C_6H_5)_2C_3N_3N=P(C_6H_5)_2C_6H_4CH-CH_2 \right]_x \left[(C_6H_5)C_3N_3 \left[N=P(C_6H_5)_2C_6H_4CH-CH_2 \right]_2 \right]_y$

Soluble portion, Run 44, Table V

TGA

RUN. NO. 202 DATE 4 Dec 74

OPERATOR F.S.
SAMPLE Insoluble Polymer
$(\phi O)_2 P(O)N_3 - 60$ 1-14-135-3
  TMA -20
  TDA -20
ATM Air ε
FLOW RATE 67 ml/min

T-AXIS	DTA-DSC	TGA	TMA	X
SCALE, °C/in 50	SCALE, °C/in___	SCALE, mg/in 1.0	SCALE, mils/in___	
PROG. RATE, °C/min 5	(mcal/sec)/in___	SUPPRESSION, mg 0 (20)	MODE___	
HEAT ✓ COOL___ ISO___	WEIGHT, mg___	WEIGHT, mg 10.21	SAMPLE SIZE___	
SHIFT, in 0	REFERENCE___	TIME CONST., sec 1.0	LOAD, g___	
		dY, (mg/min)/in 0.2	dY,(10X),(mils/min)/in___	

99'

MEASURED VARIABLE

TEMPERATURE, °C (CHROMEL / ALUMEL)

Figure 19:

TGA of $\left[(C_6H_5O)_2 P(O)N=P(C_6H_5)_2 C_6H_4 CH-CH_2 \right]_{6x} \left[(C_6H_5)_2 C_3N_3 N=P(C_6H_5)_2 C_6H_4 CH-CH_2 \right]_{2x} \left[(C_6H_5)C_3N_3 \left[N=P(C_6H_5)_2 C_6H_4 CH-CH_2 \right]_2 \right]_{1x}$

Run 43, Table V.

TGA
RUN NO. 225 DATE 5 Feb 75

OPERATOR F.S.
SAMPLE Insoluble Polymer
bulk 60/33/25
1-74-69-3
[(C₆H₅O)₂...]₃₂[TMA]₃₂[TDA]₂.₅
ATM AIR

FLOW RATE 67 ml/min

T-AXIS	DTA-DSC	TGA	TMA	
SCALE, °C/in 50	SCALE, °C/in	SCALE, mg/in 1.0	SCALE, mils/in	
PROG RATE, °C/min 5	(mcal/sec)/in	SUPPRESSION, mg 0(20)	MODE	
HEAT ✓ COOL ISO	WEIGHT, mg	WEIGHT, mg 10.92	SAMPLE SIZE	
SHIFT, in 0	REFERENCE	TIME CONST., sec 1	LOAD, g	
		dY, (mg/min)/in 0.2	dY,(10X),(mils/min)/in	

MEASURED VARIABLE

TEMPERATURE, °C (CHROMEL / ALUMEL)

Figure 20:

TGA of $[(C_6H_5O)_2P(O)N=P(C_6H_5)_2C_6H_4CH-CH_2]_{6x}[(C_6H_5)_2C_3N_3N=P(C_6H_5)_2C_6H_4CH-CH_2]_{3.3x}[(C_6H_5)C_3N_3[N=P(C_6H_5)_2C_6H_4CH-CH_2]_2]_{0.35x}$

Run 46, Table V

67

TGA

RUN NO 129 DATE 30JAN74

OPERATOR N

SAMPLE

$(\phi O)_2 P(O)N_3$ + polymer
127557 dried

ATM AIR

FLOW RATE 67ml/min

T-AXIS

SCALE, °C/in **50**

PROG RATE, °C/min **5**

HEAT ✓ COOL ISO

SHIFT, in **0**

OTA-DSC

SCALE, °C/in

[mcal/sec]/in

WEIGHT, mg

REFERENCE

TGA

SCALE, mg/in **1·0**

SUPPRESSION, mg **0(20)**

WEIGHT, mg **10·74**

TIME CONST, soc **1**

dY, [mg/min]/in **0·2**

TMA

SCALE, mils/in

MODE

SAMPLE SIZE

LOAD, g

dY,[10X],[mils/min]/in

see note
A→K 1·74

DUPONT Instruments

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MEASURED VARIABLE

TEMPERATURE, °C [CHROMEL / ALUMEL]

Figure 21

TGA of $\left[(C_6H_5O)_2 P(O)N=P(C_6H_5)_2 C_6H_4 CH-CH_2 \right]_x$

Run A, Table VIII

TGA

RUN NO. 164 DATE 27 JUN 74

OPERATOR N

SAMPLE 1-74-56-5

ATM AIR c

FLOW RATE 67 l/m

T-AXIS

SCALE, °C/in 50

PROG. RATE, °C/min

HEAT___COOL___ISO

SHIFT, in 0

DTA-DSC

SCALE, °C/in

[mcal/sec]/in

WEIGHT, mg

REFERENCE

TGA

SCALE, mg/in 1.0

SUPPRESSION, mg 0(70)

WEIGHT, mg 11.78

TIME CONST., sec 1

dY, (mg/min) /in 0.2

TMA

SCALE, mils/in

MODE
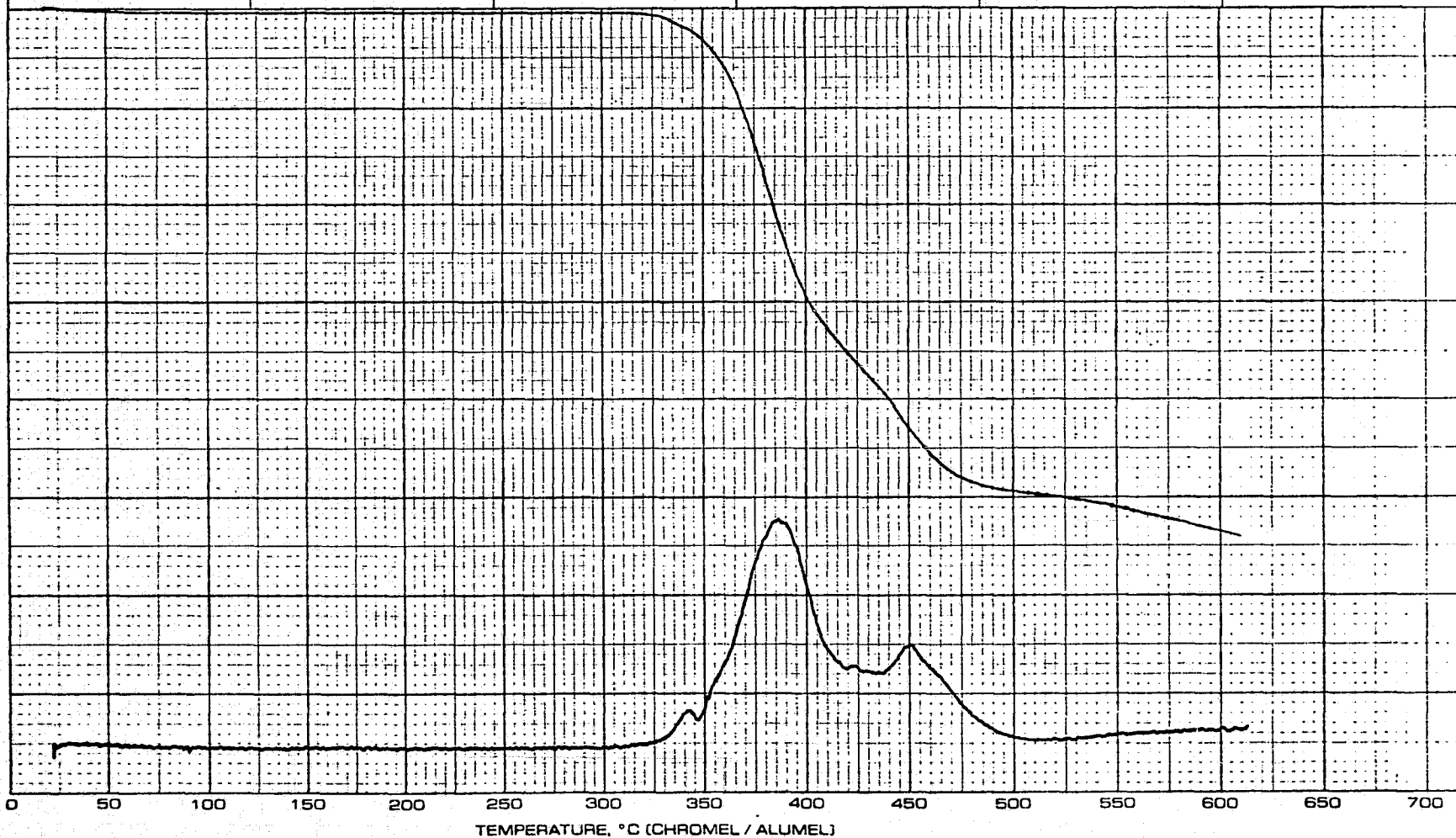
SAMPLE SIZE

LOAD, g

dY, (10X), (mils/min)/in

dried on 100°C

MEASURED VARIABLE

TEMPERATURE, °C (CHROMEL / ALUMEL)

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Figure 22:

TGA of $\left[(C_6H_5)_2P(O)N=P(C_6H_5)_2C_6H_4CH-CH_2\right]_{19.07x}$ $\left[(C_6H_5)_2C_3N_3N=P(C_6H_5)_2C_6H_4CH-CH_2\right]_{1.00x}$

Run B, Table VIII

TGA RUN NO. 162 DATE 26 Jun 74	T-AXIS	DTA-DSC	TGA	TMA	
OPERATOR N	SCALE, °C/in 50	SCALE, °C/in	SCALE, mg/in 1.0	SCALE, mils/in	[O₂?HCl?] + t₆P?N₃ + t₆...
SAMPLE: 1-74-62-2	PROG. RATE, °C/min 5	(mcal/sec)/in	SUPPRESSION, mg 0(20)	MODE	+ P₆C₂N₃(N₃)? ...
	HEAT ✓ COOL ISO	WEIGHT, mg	WEIGHT, mg 10.27	SAMPLE SIZE	
ATM Air	SHIFT, in 0	REFERENCE	TIME CONST., sec 1	LOAD, g	
FLOW RATE 67 ml/m			dY, (mg/min)/in 0.2	dY,(10X),(mils/min)/in	

MEASURED VARIABLE

TEMPERATURE, °C (CHROMEL / ALUMEL)

Figure 23:

TGA of $[(C_6H_5)_2P(O)N=P(C_6H_5)_2C_6H_4CH-CH_2]_{6.00x}$ $[(C_6H_5)_2C_3N_3N=P(C_6H_5)_2C_6H_4CH-CH_2]_{2.00x}$ $[(C_6H_5)C_3N_3[N=P(C_6H_5)_2C_6H_4CH-CH_2]_2]_{1.00x}$

Run C, Table VIII

TGA

RUN NO 168 DATE 2 AUG 74

OPERATOR W

SAMPLE

1-74-84-2 (φ PO)N₃ 80%

ATM AIR @

FLOW RATE 67 ml/min

T-AXIS

SCALE. °C/in 50

PROG. RATE. °C/min 5

HEAT ✓ COOL ___ ISO

SHIFT. in 0

DTA-DSC

SCALE. °C/in ___

(mcal/sec)/in ___

WEIGHT. mg ___

REFERENCE ___

TGA

SCALE. mg/in 1.0

SUPPRESSION, mg 0(20)

WEIGHT. mg 10.25

TIME CONST.. sec 1

dY. (mg/min)/in 0.2

TMA

SCALE. mils/in ___

MODE ___

SAMPLE SIZE ___

LOAD. g ___

dY.(10X).(mils/min)/in ___

DUPONT Instruments

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MEASURED VARIABLE

TEMPERATURE, °C (CHROMEL / ALUMEL)

Figure 24:

TGA of $\left[(C_6H_5)_2P(O)N=P(C_6H_5)_2C_6H_4CH-CH_2\right]_{8.00x}\left[(C_6H_5)_2C_3N_3N=P(C_6H_5)_2C_6H_4CH-CH_2\right]_{1.50x}\left[(C_6H_5)C_3N_3\left[N=P(C_6H_5)_2C_6H_4CH-CH_2\right]_2\right]_{0.25x}$

Run D. Table VIII

PART NO. 990088

TGA RUN NO _163_ DATE _27 JUNE 74_	T-AXIS	DTA-DSC	TGA	TMA	
OPERATOR _N_	SCALE, °C/in _50_	SCALE, °C/in	SCALE, mg/in _1.0_	SCALE, mils/in	
SAMPLE _1-74-64-1_	PROG. RATE, °C/min	(mcal/sec)/in	SUPPRESSION, mg _0(70)_	MODE	
	HEAT___COOL___ISO___	WEIGHT, mg	WEIGHT, mg _10.20_	SAMPLE SIZE	
ATM _AIR_ @	SHIFT, in _0_	REFERENCE	TIME CONST., sec _1_	LOAD, g	
FLOW RATE _67 µL/m_			dY, (mg/min)/in _0.2_	dY,(10X),(mils/min)/in	

MEASURED VARIABLE

TEMPERATURE, °C (CHROMEL / ALUMEL)

Figure 25:

TGA of $\left[(C_6H_5O)_2P(O)N=P(C_6H_5)_2C_6H_4CH-CH_2\right]_{6.00x}\left[(C_6H_5)_2C_3N_3N=P(C_6H_5)_2C_6H_4CH-CH_2\right]_{2.00x}\left[(C_6H_5)C_3N_3\left[N=P(C_6H_5)_2C_6H_4CH-CH_2\right]_2\right]_{1.00x}$

Run E, Table VIII

PART NO. 990088

TGA

RUN NO. *169* DATE *2 AUG 74*

OPERATOR *JJ*

SAMPLE *1-74-86-2*

80% (φo)₂P(O)N₃

ATM *AIR* @

FLOW RATE *67 ml/min*

T-AXIS

SCALE, °C/in *50*

PROG RATE, °C/min *5*

HEAT *✓* COOL ___ ISO ___

SHIFT, in *0*

DTA-DSC

SCALE, °C/in

(mcal/sec)/in

WEIGHT, mg

REFERENCE

TGA

SCALE, mg/in *1*

SUPPRESSION, mg *0(20)*

WEIGHT, mg *10.16*

TIME CONST., sec *1*

dY, (mg/min)/in *0.2*

TMA

SCALE, mils/in

MODE

SAMPLE SIZE

LOAD, g

dY,(10X),(mils/min)/in

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MEASURED VARIABLE

TEMPERATURE, °C (CHROMEL / ALUMEL)

Figure 26:

TGA of $\left[(C_6H_5O)_2P(O)N=P(C_6H_5)_2C_6H_4CH-CH_2\right]_{8.00x}$ $\left[(C_6H_5)_2C_3N_3N=P(C_6H_5)_2C_6H_4CH-CH_2\right]_{1.50x}$ $\left[(C_6H_5)C_3N_3\left[N=P(C_6H_5)_2C_6H_4CH-CH_2\right]_2\right]_{0.25x}$

Run F, Table VIII

TGA
RUN NO 200 DATE 2 Dec 74
OPERATOR F.S.
SAMPLE (φo)₂P(O)N₃ CO
TMA 35
1-74-131-2 TDA 5
ATM Air @
FLOW RATE 67 ml/min

T-AXIS
SCALE, °C/in 50
PROG. RATE, °C/min 5
HEAT ✓ COOL ISO
SHIFT, in 0

DTA-DSC
SCALE, °C/in
(mcal/sec)/in
WEIGHT, mg
REFERENCE

TGA
SCALE, mg/in 1.0
SUPPRESSION, mg 0(30)
WEIGHT, mg 8.97
TIME CONST., sec 1.0
dY, (mg/min)/in 0.2

TMA
SCALE, mils/in
MODE
SAMPLE SIZE
LOAD, g
dY,(10X),(mils/min)/in

✓

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MEASURED VARIABLE

TEMPERATURE, °C (CHROMEL / ALUMEL)

Figure 27:

TGA of $\overline{[(C_6H_5O)_2P(O)N=P(C_6H_5)_2C_6H_4CH-CH_2}]_{6.00x} \overline{[(C_6H_5)_2C_3N_3N=P(C_6H_5)_2C_6H_4CH-CH_2}]_{3.50x} \overline{[(C_6H_5)C_3N_3(N=P(C_6H_5)_2C_6H_4CH-CH_2}]_{2}]_{0.25x}$

Run G, Table VIII

Figure 28:

TGA of $\left[(C_6H_5O)_2P(O)N=P(C_6H_5)_2C_6H_4CH-CH_2\right]_{5.00x}\left[(C_6H_5)_2C_3N_3N=P(C_6H_5)_2C_6H_4CH-CH_2\right]_{4.00x}\left[(C_6H_5)C_3N_3\left[N=P(C_6H_5)_2C_6H_4CH-CH_2\right]_2\right]_{0.35x}$

Run H, Table VIII

TGA

RUN NO. **226** DATE II Feb 75

OPERATOR _____ F.S. _____
SAMPLE. 1-74-150-1
Solution Polymer 60/33/3.5
(6-50-2(5?m∂(70N)₃₅
ATM _air_ @
FLOW RATE _67 ml/min_

T-AXIS
SCALE. °C/in __50__
PROG. RATE, °C/min __5__
HEAT _✓_ COOL ___ ISO ___
SHIFT, in ___ 0 ___

DTA-DSC
SCALE. °C/in _____
(mcal/sec)/in _____
WEIGHT. mg _____
REFERENCE _____

TGA
SCALE, mg/in __1.0__
SUPPRESSION, mg _0(20)_
WEIGHT, mg __11.02__
TIME CONST., sec __1__
dY. (mg/min)/in __0.2__

TMA
SCALE, mils/in _____
MODE _____
SAMPLE SIZE _____
LOAD, g _____
dY.(10X),(mils/min)/in _____

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MEASURED VARIABLE

TEMPERATURE, °C (CHROMEL / ALUMEL)

Figure 29:

$$\text{TGA of } \left[(C_6H_5O)_2P(O)N=P(C_6H_5)_2C_6H_4CH-CH_2 \right]_{6.00x} \left[(C_6H_5)_2C_3N_3N=P(C_6H_5)_2C_6H_4CH-CH_2 \right]_{3.30x} \left[(C_6H_5)C_3N_3 \left[N=P(C_6H_5)_2C_6H_4CH-CH_2 \right]_2 \right]_{0.35x}$$

Run I , Table VIII